

Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v -representability problem

(Hohenberg-Kohn/Hartree-Fock/geminals/exchange-correlation)

MEL LEVY

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Communicated by Robert G. Parr, September 19, 1979

ABSTRACT Universal variational functionals of densities, first-order density matrices, and natural spin-orbitals are explicitly displayed for variational calculations of ground states of interacting electrons in atoms, molecules, and solids. In all cases, the functionals search for constrained minima. In particular, following Percus

$$Q[\rho] = \min \langle \Psi_\rho | \hat{T} + \hat{V}_{ee} | \Psi_\rho \rangle$$

is identified as the universal functional of Hohenberg and Kohn for the sum of the kinetic and electron-electron repulsion energies of an N -representable trial electron density ρ . $Q[\rho]$ searches all antisymmetric wavefunctions Ψ_ρ which yield the fixed ρ . $Q[\rho]$ then delivers that expectation value which is a minimum. Similarly,

$$W[\gamma] = \min \langle \Psi_\gamma | \hat{V}_{ee} | \Psi_\gamma \rangle$$

is shown to be the universal functional for the electron-electron repulsion energy of an N -representable trial first-order density matrix γ , where the actual external potential may be nonlocal as well as local. These universal functions do not require that a trial function for a variational calculation be associated with a ground state of some external potential. Thus, the v -representability problem, which is especially severe for trial first-order density matrices, has been solved. Universal variational functionals in Hartree-Fock and other restricted wavefunction theories are also presented. Finally, natural spin-orbital functional theory is compared with traditional orbital formulations in density functional theory.

This paper addresses the problem of generating adequate representations of the electronic structure of atoms, molecules, and solids without explicit recourse to many-particle wavefunctions. Instead, electron densities and first-order density matrices (one-matrices) are used directly for ground-state variational calculations. Densities and one-matrices are computationally attractive because their dimensions are smaller than those of the full wavefunctions.

Formal justification for utilizing the three-dimensional electron density directly in variational calculations arises from the important theorems of Hohenberg and Kohn (1). Consider N electrons in a local external potential $\hat{v}$. The Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N \hat{v}(i) \quad [1]$$

where $\hat{T}$ and $\hat{V}_{ee}$ are, respectively, the kinetic and electron-electron repulsion operators. Assume that one wishes to solve variationally for the ground-state energy of $\hat{H}$. Hohenberg and Kohn proved (1) that for this purpose there exists a valid universal functional, $F[\rho]$, which delivers the sum of the kinetic and electron-electron repulsion energies of each trial electron density ρ .

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The $F[\rho]$ of Hohenberg and Kohn is defined only for those trial ρ that are v -representable. A v -representable* ρ is one that is associated with an antisymmetric ground-state wave function of some Hamiltonian $\hat{H}'$ with local external potential $\hat{v}'$. Specifically, $\hat{H}'$ is formed from $\hat{H}$ by replacing $\hat{v}$ with $\hat{v}'$ giving

$$\hat{H}' = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N \hat{v}'(i), \quad [2]$$

where $\hat{v}'$ may or may not equal $\hat{v}$.

According to Hohenberg and Kohn (1),

$F[\rho]$ = sum of the kinetic and electron-electron repulsion energies of that antisymmetric ground-state of $\hat{H}'$ that yields ρ . [3]

$F[\rho]$ is universal in that the same value is delivered for a given trial v -representable ρ no matter what external potential is actually under consideration.

A limitation of $F[\rho]$ is that it is undefined for any ρ that is not v -representable. Furthermore, Gunnarsson and Lundquist (2) stated, "As pointed out by Hohenberg and Kohn . . . it has not been proved that an arbitrary density distribution containing an integral number of electrons can be realized by some external potential. When applying the variational principle . . . one might therefore go outside . . . range of definition." (See footnote 12 of ref. 1 and footnote 35 of ref. 2.) Accordingly, a purpose of this paper is not only to explicitly display $F[\rho]$ but also to extend the domain of $F[\rho]$ to include all N -representable ρ (consult ref. 3 for abstracts of talks by the author on this subject in April 1979). Specifically, it shall be demonstrated that there exists a proper universal variational functional, called $Q[\rho]$, which delivers the sum of kinetic and repulsion energies and which does not require ρ to be v -representable, only N -representable† (4). The existence of $Q[\rho]$ justifies density functional theory for all N -representable ρ . Furthermore, it will be seen that

$$F[\rho] = Q[\rho] \quad [4]$$

when ρ is v -representable.

Natural spin-orbitals (4-12), first defined by Löwdin (6), are

* The expression " v -representability" was first used by E. G. Larson at the Boulder Theoretical Chemistry Conference, June 1975.

† An N -representable function is one that may be obtained from some antisymmetric wavefunction (4). By the definitions, it follows that N -representability is a weaker condition than v -representability. Moreover, Gilbert (5) has argued that the N -representability condition is rather easily satisfied by a trial ρ . Now, it is certainly possible that essentially all N -representable densities are v -representable with respect to some interacting Hamiltonian. A proof, however, is not in print, to my knowledge. In any case, an important part of the present article concerns one-matrices, and only a small fraction of one-matrices are v -representable.

eigenfunctions of the one-matrix. The corresponding eigenvalues are called occupation numbers. Natural spin-orbitals yield the most rapidly convergent series expansion to the one-matrix. Interest in functional theories of one-matrices and corresponding natural spin-orbitals has grown only recently. By such theories, I mean those which, in principle, lead to the exact one-matrix, $\gamma(x|x')$, natural spin-orbitals, ψ_i , and occupation numbers, n_i , of the ground-state wavefunction for the interacting system under consideration. Such theories have recently been considered by Gilbert (5), Berrondo and Goscinski (13), Parr *et al.* (14), and Donnelly and Parr (15). Donnelly and Parr (15) discussed extensively the properties of an energy functional of the one-matrix, with respect to local external potentials, and they derived the Euler equations associated with the exact ground state.

In the present paper, the proper universal variational functional of the one-matrix and corresponding natural spin-orbitals, $W[\gamma(x|x')] = W[n_i, \psi_i]$, is presented for the electron-electron repulsion energy. The interacting Hamiltonians of interest may contain nonlocal as well as local external potentials. In any case, it will be shown that the functional $W[\gamma]$ does not require v -representability, only N -representability.

It is hoped that the formal explicit displays of $Q[\rho]$ and $W[\gamma]$ will lead to accurate and computationally feasible approximations to these functionals.

$Q[\rho]$: A universal functional of the electron density

Following is the definition of $Q[\rho]$ which shall be shown to be the proper universal variational functional of all N -representable ρ for the sum of kinetic and repulsion energies:

$$Q[\rho] = \min \langle \Psi_\rho | \hat{T} + \hat{V}_{ee} | \Psi_\rho \rangle. \quad [5]$$

$Q[\rho]$ searches all antisymmetric wavefunctions Ψ_ρ which yield the fixed trial ρ , where ρ need not be v -representable. $Q[\rho]$ then delivers that expectation value which is a minimum. Furthermore, an upper bound to $Q[\rho]$ is provided by an expectation value of $\hat{T} + \hat{V}_{ee}$ with any antisymmetric Ψ which yields ρ . The definition for $Q[\rho]$ in Eq. 5 is in the spirit of Percus' recent definition (16) of a universal kinetic energy functional for independent fermion systems.

For $Q[\rho]$ to be a valid universal variational functional, it is necessary to prove the following two theorems for N -representable ρ :

THEOREM I.

$$\int d\vec{r} \hat{v}(\vec{r}) \rho(\vec{r}) + Q[\rho] \geq E_{g.s.} \quad [6]$$

THEOREM II.

$$\int d\vec{r} \hat{v}(\vec{r}) \rho_{g.s.}(\vec{r}) + Q[\rho_{g.s.}] = E_{g.s.} \quad [7]$$

where $\rho_{g.s.}$ and $E_{g.s.}$ are, respectively, a ground-state density and the ground-state energy of $\hat{H}$.

It is convenient to establish additional notations to facilitate the proofs. Namely, call $\Psi_{\min}^\rho$ that wavefunction that satisfies the righthand side of Eq. 5. Then, it follows that

$$Q[\rho] = \langle \Psi_{\min}^\rho | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^\rho \rangle \quad [8]$$

and

$$Q[\rho_{g.s.}] = \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle. \quad [9]$$

Proof of Theorem I:

By the definition in Eq. 8,

$$\begin{aligned} \int d\vec{r} \hat{v}(\vec{r}) \rho(\vec{r}) + Q[\rho] \\ = \int d\vec{r} \hat{v}(\vec{r}) \rho(\vec{r}) + \langle \Psi_{\min}^\rho | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^\rho \rangle, \end{aligned} \quad [10]$$

or, with $\hat{V} = \sum_{i=1}^N \hat{v}(i)$, it follows that

$$\int d\vec{r} \hat{v}(\vec{r}) \rho(\vec{r}) + Q[\rho] = \langle \Psi_{\min}^\rho | \hat{V} + \hat{T} + \hat{V}_{ee} | \Psi_{\min}^\rho \rangle. \quad [11]$$

But, by the variational principle,

$$\langle \Psi_{\min}^\rho | \hat{V} + \hat{T} + \hat{V}_{ee} | \Psi_{\min}^\rho \rangle \geq E_{g.s.} \quad [12]$$

Addition of the last two equations completes the proof.

Proof of Theorem II:

By the variational principle,

$$E_{g.s.} \leq \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{V} + \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle, \quad [13]$$

or

$$\begin{aligned} \langle \Psi_{g.s.} | \hat{V} + \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle \\ \leq \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{V} + \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle, \end{aligned} \quad [14]$$

or

$$\begin{aligned} \int d\vec{r} \hat{v}(\vec{r}) \rho_{g.s.}(\vec{r}) + \langle \Psi_{g.s.} | \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle \\ \leq \int d\vec{r} \hat{v}(\vec{r}) \rho_{g.s.}(\vec{r}) + \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle, \end{aligned} \quad [15]$$

which leads to

$$\langle \Psi_{g.s.} | \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle \leq \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle. \quad [16]$$

But, the definition of $\Psi_{\min}^{\rho_{g.s.}}$ dictates that

$$\langle \Psi_{g.s.} | \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle \geq \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle. \quad [17]$$

The last two equations hold simultaneously if and only if

$$\langle \Psi_{g.s.} | \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle = \langle \Psi_{\min}^{\rho_{g.s.}} | \hat{T} + \hat{V}_{ee} | \Psi_{\min}^{\rho_{g.s.}} \rangle, \quad [18]$$

or

$$\langle \Psi_{g.s.} | \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle = Q[\rho_{g.s.}]. \quad [19]$$

Now,

$$\langle \Psi_{g.s.} | \hat{V} + \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle = E_{g.s.}, \quad [20]$$

or

$$\int d\vec{r} \hat{v}(\vec{r}) \rho_{g.s.}(\vec{r}) + \langle \Psi_{g.s.} | \hat{T} + \hat{V}_{ee} | \Psi_{g.s.} \rangle = E_{g.s.} \quad [21]$$

Finally, substitution of Eq. 19 into Eq. 21 completes the proof. Furthermore, Eq. 19 implies $F[\rho] = Q[\rho]$ when ρ is v -representable. Also, observe that the possible degeneracy of $\Psi_{g.s.}$ clearly does not affect the proof. (See also footnote 3 of ref. 14.)

Observe that $\Psi_{g.s.} = \Psi_{\min}^{\rho_{g.s.}}$, which means $\Psi_{g.s.}$ may be obtained directly from $\rho_{g.s.}$ even if the external potential is unknown; find that wavefunction which yields $\rho_{g.s.}$ and minimizes the expectation value of $\hat{T} + \hat{V}_{ee}$ (3). If $\Psi_{g.s.}$ is degenerate, then all of the ground-state wavefunctions may be obtained, one at a time, by the above procedure.

Universal functionals in Hartree-Fock and in other restricted wavefunction theories

The proofs of the preceding section can be directly mapped onto the Hartree-Fock problem. The Hartree-Fock analogue to $Q[\rho]$, which shall be denoted $P[\rho]$, is

$$\begin{aligned} P[\rho] = \min \langle \Phi_\rho | \hat{T} + \hat{V}_{ee} | \Phi_\rho \rangle; \Phi_\rho \\ = \text{single determinants.} \end{aligned} \quad [22]$$

Note that Eq. 22 also enables one to abstract a Hartree-Fock ground-state wavefunction from a Hartree-Fock ground-state

density[†]. Furthermore, observe that the geminal product analogue (18) to $P[\rho]$ would require that the Φ s be restricted to geminal product wavefunctions. Similarly, Eq. 22 may be extended to any other formalism where the implied wavefunctions are restricted to have a specific structure.

$W[\gamma]$: A universal functional of the first-order density matrix and natural spin-orbitals

Following is the definition of $W[\gamma(x|x')]$ which is the proper universal variational functional of all N -representable $\gamma(x|x')$ for the repulsion energy:

$$W[\gamma(x|x')] = \min \langle \Psi_\gamma | \hat{V}_{ee} | \Psi_\gamma \rangle. \quad [23]$$

$W[\gamma]$ searches all antisymmetric wavefunctions Ψ_γ that yield the fixed trial γ , where γ need not be v -representable. $W[\gamma]$ then delivers that expectation value which is a minimum.

$W[\gamma]$ is a valid universal functional for all N -representable γ in that the following conditions are satisfied:

$$E_{g.s.} \leq \int dx [-\frac{1}{2}\nabla^2 + v]\gamma(x|x') + W[\gamma(x|x')] \quad [24]$$

and

$$E_{g.s.} = \int dx [-\frac{1}{2}\nabla^2 + \hat{v}]\gamma_{g.s.}(x|x') + W[\gamma_{g.s.}(x|x')]. \quad [25]$$

The assertions made in Eqs. 24 and 25 will not be proved because the proofs are analogous to those of *Theorems I and II*. Observe that the external potential $\hat{v}$ may be nonlocal as well as local and that a spin-dependent Hamiltonian may be used. Therefore, Eq. 23 unifies several formulations (5, 13–15, 19, 20). Also, note that $\Psi_{v_{g.s.}}$ can be degenerate.

Eqs. 24 and 25 imply a corresponding natural spin-orbital functional theory (5, 14, 15). Substitution of $\gamma(x|x') = \sum_i n_i \Psi_i(x)\Psi_i(x')$ into Eqs. 24 and 25 gives

$$E_{g.s.} \leq \sum_i n_i \int dx \Psi_i(x)^* [-\frac{1}{2}\nabla^2 + \hat{v}] \Psi_i(x) + W[n_i, \Psi_i] \quad [26]$$

and

$$E_{g.s.} = \sum_i n_i^{\dagger s} \int dx \Psi_i^{\dagger s}(x)^* [-\frac{1}{2}\nabla^2 + \hat{v}] \Psi_i^{\dagger s}(x) + W[n_i^{\dagger s}, \Psi_i^{\dagger s}]. \quad [27]$$

For N -representability with respect to a pure state, it is necessary but not sufficient (4–11) that $0 \leq n_i \leq 1$. In any case, minimization of Eq. 26 by proper optimizations of the n_i s and Ψ_i s yields the exact ground-state energy with the corresponding set of exact occupation numbers and natural spin-orbitals.

Traditional orbital formulations in density functional theory[‡]

Natural spin-orbital functional theory (5, 14, 15), as given by Eqs. 26 and 27, should be compared with traditional orbital formulations in density functional and spin-density functional theories, as developed by Slater (22, 23), Kohn and Sham (24), Gáspár (25), and others (2, 19, 20, 26). Based upon the Hohenberg–Kohn theorems (1), Kohn and Sham (24) helped justify these orbital formulations by deriving a set of self-consistent equations, analogous to the Hartree equations, that exactly solve the interacting fermion problem. The Kohn–Sham formalism

yields, in principle, the exact $E_{g.s.}$ and $\rho_{g.s.}$. The computational results have been generally encouraging and, at times, impressive (see, for instance, references 2, 23, and 27–34). Unlike Eq. 27, these formalisms, however, neither yield exact ground-state one-matrices nor their corresponding set of exact natural spin-orbitals. In particular, the Kohn–Sham one-matrix[¶] does not equal $N \int \Psi_{g.s.}^{*}(1', 2, \dots, N) \Psi_{g.s.}(1, 2, \dots, N) dx_2 \dots dx_N$.

Concluding remarks

Universal variational functionals of densities, one-matrices, and natural spin-orbitals have been explicitly displayed by Eqs. 5, 22, and 23. *These equations have similar structures. Existing functional theories are thereby united. In all cases, the functionals search for constrained minima.* Accurate approximations to the functionals must be parameterized to duplicate these searches.

The v -representability problem has been solved. One can now confidently use existing Euler equations without being concerned about whether or not the functions in the immediate neighborhood of the optimum functions are v -representable. (Consult footnote 35 of ref. 2). The v -representability constraint is particularly severe if the trial function is a one-matrix. Only a small fraction of one-matrices are v -representable. In particular, if more than one density matrix yields a v -representable density with respect to a nondegenerate ground state, then by Hohenberg and Kohn (1), only one of these density matrices can be v -representable (15). For instance, no idempotent one-matrix is v -representable. It is fortunate, indeed, that v -representability is not required after all.

Eq. 23 unifies several one-matrix functional theories. For a variational calculation involving a local external potential, Donnelly and Parr (15) proved that $W[\gamma]$ exists by demonstrating that its existence is implied in the original Hohenberg–Kohn theorem (1). Berrondo and Goscinski (13) added a nonlocal external potential to the N -body Hamiltonian and then obtained a variational principle involving the one-matrix for a local external potential by eliminating the nonlocal external source. Gilbert (5) proved the existence of $W[\gamma]$ for a nonlocal external potential by extending the original Hohenberg–Kohn theorem to the nonlocal situation. *The present paper identifies Eq. 23 as the universal functional implied in all three of the above theories.*

Perhaps we should actively search for approximations to that universal functional of $\gamma(x|x')$ which is displayed in Eq. 23. It might turn out that accurate computationally useful approximations to $W[\gamma]$ are possible because $W[\gamma]$ appears to be less complicated, in a formal sense, than either $Q[\rho]$ or the exchange-correlation functional (24), $E_{xc}[\rho]$. In particular, $W[\gamma]$ does not contain any kinetic energy, while it can be shown that $E_{xc}[\rho]$ in traditional orbital formulations must contain a small positive kinetic energy contribution, and $Q[\rho]$ must, of course, contain all the kinetic energy. Also, more information is contained in γ than in ρ . On the other hand, γ itself is more complicated than ρ and it is somewhat more difficult to keep γ N -representable (37).

I thank Dr. R. G. Parr and his research group, Drs. J. P. Perdew, J. Harris, W. E. Palke, G. Handler, D. W. Smith, M. Frucht, and the referees, for their interest, valuable discussions, and suggestions.

[‡] While the present paper was being refereed, an article (17) by P. W. Payne appeared, entitled "Density Functionals in Unrestricted Hartree-Fock Theory," where ideas similar to Eq. 22 were put forth.

[§] It should be pointed out that a new orbital functional theory has recently been proposed which corrects the local spin-density approximation for exchange and correlation by subtracting the residual self-interaction of each orbital (21).

[¶] A density matrix method has been put forth recently (35, 36). This method, however, is in the spirit of the Kohn–Sham formulation in that idempotent one-matrices are generated. The exact ground-state one-matrix, therefore, is not obtained because the latter cannot be idempotent.

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