Density Functionals for the Energy of Electronic Systems: Explicit Variational Construction

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(Received 9 December 1987)

A nonlinear transformation performs the Levy-constrained search formulation of the density functional for the electronic energy through a minimization of the energy with respect to a set of variational coefficients. The construction requires a complete set of arbitrary functions as the auxiliary basis. Truncation of the basis set provides an upper bound to the energy functional. Practical approaches to obtain accurate upper bounds to this functional are discussed, and a density-functional alternative to the standard Hartree-Fock method is described.

PACS numbers: 31.15.+q, 02.30.+g, 03.65.Ge

The celebrated paper of Hohenberg and Kohn[1] marked the advent of density-functional theory. However, the first practical realization of the density functional for the energy of fermionic systems has been put forward by Levy.[2] The Levy construction defines the density functional for the electronic energy $E[\rho]$ as the minimum of the expectation value $\langle\Psi|\hat{H}|\Psi\rangle$ over all the many-electron wave functions Ψ that yield the proper density, $\Psi\rightarrow\rho(r)$. The main problem with the Levy-constrained search is to generate all suitable many-electron functions.

Zumbach and Maschke[3] have proposed the construction of the Levy density functional based on the representation of the many-electron wave function by a complete set of Slater determinants. Unfortunately, their approach turned out to be invalid because of an erroneous omission of the off-diagonal elements in the electron density [see Eq. (8) in the following]. It should be also pointed out that the use of the Harriman orbitals[3] for construction of the Slater determinants is an unoptimal choice, for they do not resemble Hartree-Fock orbitals.

In the present paper I report the construction of all the many-electron functions that are admissible in the Levy-constrained search. I aim first at constructing a set of orthonormal one-electron wave functions (orbitals) that, when used to build the many-determinantal wave function, yield the proper electron density. For this purpose I introduce a vector

$$\boldsymbol{\phi}(r)=[\phi_1(r),\phi_2(r),\ldots] \qquad (1)$$

of finite-valued continuous basis functions. These functions are supposed to form a complete set, but *do not* have to be orthogonal or normalized. For clarity, vectors in the Hilbert space are denoted by boldface, while the coordinate vector r is left in italic type. For simplicity, in the following I assume an occupancy of one electron per orbital. The Einstein summation convention is used.

Let

$$\boldsymbol{\psi}(r)=[\psi_1(r),\psi_2(r),\ldots] \qquad (2)$$

be a vector of orthonormal, linearly independent, finite-valued, continuous functions. Again, these functions are supposed to form a complete set. We construct all the Slater determinants $|P\rangle$, $|Q\rangle,\ldots$ from the orbitals $\psi(r)$. According to the Löwdin theorem,[4] the set composed of all these determinants is complete in the many-electron space. The exact many-electron wave function of the ground state is a linear combination of the Slater determinants

$$|\Psi\rangle=C^P|P\rangle,\quad C^PC_P=1, \qquad (3)$$

with the vector C^P minimizing $\langle\Psi|\hat{H}|\Psi\rangle$.

To calculate the electron density corresponding to Ψ, we observe that for any one-electron operator $\hat{O}$ we have

$$\langle P|\sum_{i=1}^{N}\hat{O}(i)|Q\rangle=\Xi_{PQ}^{kl}O_{kl}, \qquad (4)$$

with

$$O_{kl}=\langle\psi_k(1)|\hat{O}(1)|\psi_l(1)\rangle; \qquad (5)$$

whereas for any two-electron operator

$$\langle P|\sum_{i>j=1}^{N}\hat{O}(i,j)|Q\rangle=\tfrac{1}{2}\,\Omega_{PQ}^{klmn}O_{klmn}, \qquad (6)$$

with

$$O_{klmn}=\langle\psi_k(1)\psi_l(2)|\hat{O}(1,2)|\psi_m(1)\psi_n(2)\rangle. \qquad (7)$$

The tensors of coupling coefficients, Ξ and Ω, are computed according to the Slater-Condon rules.[5] As a special case of Eq. (4) we arrive at

$$\rho(r)=C^PC^Q\Xi_{PQ}^{kl}\psi_k(r)\psi_l(r). \qquad (8)$$

It is now clear that the transformation

$$\psi_k(r)=f^{1/2}(r)s_k^u\phi_u(r), \qquad (9)$$

with s and $f(r)$ calculated self-consistently from

$$\mathsf{s}=\mathsf{S}^{-1/2}, \qquad (10)$$

$$f(r)=\rho(r)[C^PC^Q\Xi_{PQ}^{kl}s_k^us_l^v\phi_u(r)\phi_v(r)]^{-1}, \qquad (11)$$

and

$$S_j^i = \int f(r)\phi^i(r)\phi_j(r)d^3r, \tag{12}$$

relates an arbitrary complete set of one-electron functions $\phi(r)$ to the orthonormal set $\psi(r)$ that, through the many-electron function (3), yields the proper density. Both the existence of matrix s and a linear convergence of the iterative process, Eqs. (10)–(12), can be proven.[6] For a fixed density, the many-electron function that results in the minimum of the electronic energy (and thus in the density functional $E[\rho]$) is reached through a minimization of the variational coefficients C^P.

The explicit form of the density functional for the electronic energy reads

$$E[\rho] = \min_{C^P}\left[\int v(r)\rho(r)d^3r + \langle T\rangle + \langle V_{ee}\rangle\right] = \int v(r)\rho(r)d^3r + \langle T\rangle^{(1)} + \langle V_{ee}\rangle^{(1)} + \min_{C^P}[\langle T\rangle^{(2)} + \langle V_{ee}\rangle^{(2)}]. \tag{13}$$

In this equation $v(r)$ is the external potential, $\langle T\rangle^{(1)}$ is the Weizsäcker kinetic energy[7]

$$\langle T\rangle^{(1)} = \tfrac{1}{8}\int |\nabla\rho(r)|^2\rho^{-1}(r)d^3r, \tag{14}$$

and $\langle V_{ee}\rangle^{(1)}$ is the classical Coulomb electronic repulsion energy

$$\langle V_{ee}\rangle^{(1)} = \tfrac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}d^3r_1d^3r_2. \tag{15}$$

The variational part of $E[\rho]$ contains two components: The kinetic energy

$$\langle T\rangle^{(2)} = \tfrac{1}{2}\int f(r)[C^PC^Q\Xi_{PQ}^{kl}s_k^us_l^v\nabla\phi_u(r)\cdot\nabla\phi_v(r)]d^3r - \tfrac{1}{2}\int f^2(r)|C^PC^Q\Xi_{PQ}^{kl}s_k^us_l^v\phi_u(r)\nabla\phi_v(r)|^2\rho^{-1}(r)d^3r, \tag{16}$$

and the component that incorporates the electron correlation (including exchange),

$$\langle V_{ee}\rangle^{(2)} = \tfrac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}h(r_1,r_2)d^3r_1d^3r_2, \tag{17}$$

with the correlation function

$$h(r_1,r_2) = -1 + f(r_1)f(r_2)\rho^{-1}(r_1)\rho^{-1}(r_2)[C^PC^Q\Omega_{PQ}^{klmn}s_k^us_l^vs_m^ts_n^w\phi_u(r_1)\phi_v(r_2)\phi_t(r_1)\phi_w(r_2)]. \tag{18}$$

The variational part of $E[\rho]$ can be minimized by application of a standard differential calculus. Atomic units were used in Eqs. (13)–(18).

I have succeeded in performing the Levy-constrained search through a minimization of the energy, Eq. (13), with respect to the vector C^P. This yields the exact functional as long as the complete set of functions, Eq. (1), is used. For the electronic systems that do not possess any high point symmetry of the external potential, the set $\{x^ky^lz^m,\ k,l,m = 0,1,\ldots\}$ would be an excellent choice for $\boldsymbol{\phi}(r)$. Any truncation of $\boldsymbol{\phi}(r)$ will result in an upper bound to $E[\rho]$. The functional $E[\rho]$ provides also the ground-state energy which is obtained by its minimization with respect to $\rho(r)$.

Let us discuss now the particular case of $|\Psi\rangle$ being a single-determinantal wave function. The vectors $\boldsymbol{\psi}(r)$ and $\boldsymbol{\phi}(r)$ have now only N components, where N is the number of electrons. Equations (8) and (11) are greatly simplified:

$$\rho(r) = \psi_k(r)\psi_k(r), \tag{19}$$

$$f(r) = \rho(r)[(\mathrm{S}^{-1})_{kl}\phi_k(r)\phi_l(r)]^{-1}. \tag{20}$$

The corresponding electronic energy is given now by a Hartree-Fock (HF) functional:

$$E_{\mathrm{HF}}[\rho] = \min_{\boldsymbol{\psi}(r)}[E_{\mathrm{HF}}(\boldsymbol{\psi})] = \min_{\boldsymbol{\psi}(r)}\left[\sum_{i=1}^N\langle\psi_i|\hat{V}+\hat{T}|\psi_i\rangle + \tfrac{1}{2}\sum_{i=1}^N\langle\psi_i|\hat{J}+\hat{K}|\psi_i\rangle\right], \tag{21}$$

where $\hat{V}$, $\hat{T}$, $\hat{J}$, and $\hat{K}$ are the external potential, the kinetic energy, and the Coulomb and the exchange operators, respectively. The minimization is carried out over all the vectors $\boldsymbol{\psi}(r)$ that satisfy Eq. (19). One should recall that the external potential and Coulomb parts do not depend on the choice of $\boldsymbol{\psi}(r)$. Therefore one can restrict the minimization to the kinetic and exchange energies.

The transform (9) enables us to replace the constrained search of Levy by an unconstrained minimization over all possible vectors $\boldsymbol{\phi}(r)$. The very fact that now we have no constraints on the vector $\boldsymbol{\phi}(r)$ enables us to use an ordinary variational calculus for finding the HF energy functional, Eq. (21). The variational part of the kinetic energy and the exchange energy, Eqs. (16)–(18), read

$$\langle T\rangle^2=\tfrac{1}{2}\int f(r)[(\mathrm{S}^{-1})_{kl}\nabla\phi_k(r)\cdot\nabla\phi_l(r)]d^3r-\tfrac{1}{2}\int f^2(r)\,|(\mathrm{S}^{-1})_{kl}\phi_k(r)\nabla\phi_l(r)|^2\rho^{-1}(r)d^3r \tag{22}$$

and

$$\langle K\rangle=-\tfrac{1}{2}\int\int\frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}[(\mathrm{S}^{-1})_{kl}\phi_k(r_1)\phi_l(r_2)]^2 \times[(\mathrm{S}^{-1})_{kl}\phi_k(r_1)\phi_l(r_1)]^{-1}[(\mathrm{S}^{-1})_{kl}\phi_k(r_2)\phi_l(r_2)]^{-1}d^3r_1d^3r_2. \tag{23}$$

Calculating the variation of their sum with respect to $\delta\boldsymbol{\phi}(r)$, and bearing in mind that S depends on $\phi(r)$, one arrives at a set of N coupled differential-integral Hartree-Fock–type equations. Solution of these equations yields the optimal vector $\boldsymbol{\phi}(r)$ and, in turn, the HF energy functional in an explicit form. In fact, because for any nonsingular matrix C and any finite and continuous real-valued function that has no zeros, $\mu(r)$, the transformation

$$\boldsymbol{\phi}(r)\rightarrow\mu(r)\boldsymbol{\phi}(r)\mathrm{C} \tag{24}$$

leaves the value of the functional (21) unchanged; only $N-1$ equations have to be solved, for we can always set $\phi_1(r)\equiv 1$. Eventually, another equation that arises from the variation with respect to $\delta\rho(r)$ has to be solved to obtain the ground-state electron density and the corresponding Hartree-Fock energy.

For lack of space I do not give here an explicit form of the variational equations (they will be published elsewhere[6]). They are complicated and probably, like HF equations, are not easy to solve for large molecular systems. There is, however, another route to obtain approximate density functionals for the HF energy. One should note that most of the important features of the electronic wave function (like the cusp properties at the divergence points of the external potential and asymptotics for large distances) can be readily incorporated in a trial electron density. Unlike in the HF method, in which *the orbitals are used to generate the electron density* and therefore should bear a substantial accuracy to provide a reasonable HF energy, the present formulation is quite insensitive to the choice of the basis functions $\boldsymbol{\phi}(r)$, *as long as they possess a proper symmetry.* The resulting energy is, of course, an upper limit to the exact $E_{\mathrm{HF}}[\rho]$.

I envision that the present development can have a substantial impact on electronic structure calculations. The electron density can be easily represented by its values at the nodes of some grid in the Cartesian space, while the generating set, $\boldsymbol{\phi}(r)$, can be represented analytically by very simple functions. This would result in a tremendous improvement in accuracy versus CPU time ratio for Hartree-Fock calculations.

Because of its simplicity, I believe that the present approach can find several applications in quantum chemistry. First of all, it enables one to obtain wave functions (exact or approximate) and ground-state energies directly from electron densities (calculated or experimental). It can be also a starting point for several approximations and bounds to $E[\rho]$.

The author is indebted to Professor Robert G. Parr for asking "tough" questions. This research was supported by a grant to the University of North Carolina from the National Science Foundation.

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