Direct Calculation of Electron Density in Density-Functional Theory

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A new approach for the study of ground states of many-electron systems is developed via direct calculation of the density in density-functional theory. Not using the Kohn-Sham equations, the method divides a system into subsystems in physical space and determines the density for each subsystem. The method is demonstrated with calculations for the nitrogen molecule, which is divided into two atomic subsystems. We expect this approach to enable calculations for large molecules beyond the reach of conventional methods.

Density-functional theory (DFT) plays a role of increasing importance in the calculations of ground states of molecules and solids.[1-5] Most of the contemporary DFT calculations are based on the Kohn-Sham (KS) formulation.[6] In spite of its success, however, the application of the KS approach is limited in the size of molecules. For a molecule with N electrons, the KS approach requires $N/2$ orbitals (for closed-shell molecules) to represent the electron density, and the computational effort scales as N^3. This cubic scaling is the bottleneck for the application of DFT to large molecules.

We intend here to explore further the fundamental principle of DFT—the use of the electron density as the basic variable to describe the ground state of a many-electron system. The Thomas-Fermi (TF) and related theories were the original attempts in using the electron density as the basic variable,[1,3] based on the approximation for the kinetic-energy functional. The idea is indeed very appealing—the computational effort of such an approach would scale linearly as the size of the molecule. The accuracy of the approximate kinetic-energy functionals, however, is too poor to commend the TF-type theory as a quantitative theory of electronic structure. The recent integral formulation of KS theory in principle makes possible the systematic improvement of the TF approach,[7,8] but the complexity of many-dimensional integrations in the formulation still defies practical application.

In this Letter, we present a new method for the direct calculation of the electron density and its total energy. The method does not solve the KS equations nor is it based on an approximate kinetic-energy functional. Consider a system of N electrons in an external field $v(\mathbf{r})$. In terms of the electron density $\rho(\mathbf{r})$, the total energy can be written as[1-3]

$$E[\rho] = T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho]$$
$$+ \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' + \sum_{a,b}\frac{Z_aZ_b}{R_{ab}}, \quad (1)$$

where $T_s[\rho]$ is the kinetic energy of a noninteracting electron gas in its ground state with density ρ, $E_{xc}[\rho]$ is

the exchange-correlation energy, and the last term is the electrostatic energy of the nuclei. The minimization of the energy functional $E[\rho]$ with respect to the electron density is then accomplished if the KS equation is satisfied,

$$\hat{H}\psi_i(\mathbf{r}) = [-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \quad (2)$$

and the density is given by

$$\rho(\mathbf{r}) = 2\sum_i^{N/2}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}), \quad (3)$$

where $V_{\text{eff}}(\mathbf{r})$ is the KS effective local potential,

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + V_{xc}(\mathbf{r}), \quad (4)$$

with $V_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$. The total energy, Eq. (1), can also be expressed in terms of the KS eigenvalues:[1-3]

$$E[\rho] = 2\sum_i^{N/2}\varepsilon_i + Q[\rho] + \sum_{a,b}Z_aZ_b/R_{ab}, \quad (5)$$

where $Q[\rho] = \int\rho[-\phi(\mathbf{r})/2 - V_{xc}(\mathbf{r})]d\mathbf{r} + E_{xc}[\rho]$, and $\phi(\mathbf{r})$ is the electrostatic potential due to the electrons, which is the second term on the right-hand side of Eq. (4).

The foregoing is the conventional KS formulation. Our goal here is to bypass the KS equation (2) and to compute the electron density directly without using the $N/2$ orbitals as in Eq. (3). Rewrite Eq. (3) as[1-3]

$$\rho(\mathbf{r}) = 2\langle\mathbf{r}|\eta(\varepsilon_F - \hat{H})|\mathbf{r}\rangle, \quad (6)$$

where $\eta(x)$ is the Heaviside step function [$\eta(x) = 1$ for $x > 0$, and $\eta(x) = 0$ for $x \leq 0$], $\hat{H}$ is the KS Hamiltonian, and ε_F can be any value between the highest occupied and the lowest unoccupied eigenvalues. Now divide the system into subsystems in the physical space by the following *smooth* partition $1 = \sum_\alpha p^\alpha(\mathbf{r})$, where $p^\alpha(\mathbf{r})$ is a positive weighting function for the subsystem α. $p^\alpha(\mathbf{r})$ is large in the subspace where the subsystem α is and is small away from it. Then the total density can be exactly expressed as the sum

$$\rho(\mathbf{r}) = 2\sum_\alpha p^\alpha(\mathbf{r})\langle\mathbf{r}|\eta(\varepsilon_F - \hat{H})|\mathbf{r}\rangle = \sum_\alpha\rho^\alpha(\mathbf{r}), \quad (7)$$

where $\rho^\alpha(\mathbf{r}) = 2p^\alpha(\mathbf{r})\langle\mathbf{r}|\eta(\varepsilon_F - \hat{H})|\mathbf{r}\rangle$.

To use the above equation to calculate the electron density, we have to approximate the KS Hamiltonian. Projection of $\hat{H}$ to the space spanned by the linear combination of atomic orbitals (LCAO) is a *global* approximation to $\hat{H}$, leading to the usual LCAO approach for the KS equations. We want something different here. The smooth partition of density in Eq. (7) allows a *local* approximation to $\hat{H}$; namely, we can make different approximations to $\hat{H}$ for different subsystems. Thus, we introduce the following approximation for $\rho^\alpha(\mathbf{r})$:

$$\tilde{\rho}^\alpha(\mathbf{r}) = 2p^\alpha(\mathbf{r})\langle\mathbf{r}|f_\beta(\varepsilon_F - \hat{H}^\alpha)|\mathbf{r}\rangle, \tag{8}$$

where $f_\beta(x)$ is the Fermi function, $f_\beta(x) = [1 + \exp(-\beta x)]^{-1}$, and $\hat{H}^\alpha$ is the subspace approximation of the KS Hamiltonian operator. The Fermi function in Eq. (8) is a convenient choice to make the value of ε_F unique; the uniqueness of ε_F is necessary as will be shown below.

We now let $\hat{H}^\alpha$ be the projection of the original KS Hamiltonian operator $\hat{H}$ to the space spanned by the nonorthogonal basis functions $\{\phi_j^\alpha(\mathbf{r})\}$ that are *localized* in the subsystem α:

$$\hat{H}^\alpha = \sum_{jklm} |\phi_j^\alpha\rangle(S^\alpha)_{jk}^{-1}(H^\alpha)_{kl}(S^\alpha)_{lm}^{-1}\langle\phi_m^\alpha|$$

$$= \sum_i |\psi_i^\alpha\rangle\varepsilon_i^\alpha\langle\psi_i^\alpha|, \tag{9}$$

where $(S^\alpha)_{jk}^{-1}$ is the (j,k) element of the inverse matrix of the overlap matrix $\mathbf{S}^\alpha$, and $(H^\alpha)_{kl}$ the (k,l) element of the Hamiltonian matrix $\mathbf{H}^\alpha$, with

$$(S^\alpha)_{ij} = \langle\phi_i^\alpha|\phi_j^\alpha\rangle, \quad (H^\alpha)_{ij} = \langle\phi_i^\alpha|\hat{H}|\phi_j^\alpha\rangle. \tag{10}$$

In Eq. (9), the first equality is a standard projection, while the second expresses the projected Hamiltonian $\hat{H}^\alpha$ in terms of its eigenvalues $\{\varepsilon_i^\alpha\}$ and eigenfunctions $\{\psi_i^\alpha\}$. The eigenfunctions $\{\psi_i^\alpha\}$ are obtained as the linear combinations of the basis functions $\{\phi_j^\alpha\}$,

$$\psi_i^\alpha(\mathbf{r}) = \sum_j C_{ji}^\alpha\phi_j^\alpha(\mathbf{r}), \tag{11}$$

where the linear coefficients are the solutions of the following generalized eigenvalue equation derived from the Rayleigh-Ritz variational principle:

$$(\mathbf{H}^\alpha - \varepsilon_i^\alpha\mathbf{S}^\alpha)\mathbf{C}_i^\alpha = 0, \tag{12}$$

where the matrices involved are given in Eq. (10). With $\{\psi_i^\alpha, \varepsilon_i^\alpha\}$ given by Eqs. (11) and (12), one can easily verify the equivalence of the two expressions for $\hat{H}^\alpha$ in Eq. (9).

Using the spectral resolution of $\hat{H}^\alpha$ in Eq. (9), we can evaluate the subspace density ρ^α by Eq. (8). Then by Eq. (7), we obtain the expression for the direct calculation of the total electron density

$$\tilde{\rho}(\mathbf{r}) = 2\sum_\alpha p^\alpha(\mathbf{r})\sum_i f_\beta(\varepsilon_F - \varepsilon_i^\alpha)|\psi_i^\alpha(\mathbf{r})|^2, \tag{13}$$

where the value of ε_F is determined by the normalization constraint

$$N = \int\tilde{\rho}(\mathbf{r})d\mathbf{r} = 2\sum_\alpha\sum_i f_\beta(\varepsilon_F - \varepsilon_i^\alpha)\langle\psi_i^\alpha|p^\alpha|\psi_i^\alpha\rangle. \tag{14}$$

To guarantee a unique solution of ε_F for a given N, it is necessary to keep a finite β so that the right-hand side of Eq. (14) is a continuous monotonic function of ε_F. The value of β can be chosen such that its increase does not significantly change the total energy.

We also need to determine the eigenvalue summation in the expression for total energy, Eq. (5); namely,

$$\mathcal{E} = 2\sum_i^{N/2}\varepsilon_i = 2\int d\mathbf{r}\langle\mathbf{r}|\hat{H}\eta(\varepsilon_F - \hat{H})|\mathbf{r}\rangle. \tag{15}$$

Now make an approximation to Eq. (15) in a similar fashion as in Eq. (8), namely,

$$\tilde{\mathcal{E}} = 2\int d\mathbf{r}\sum_\alpha p^\alpha(\mathbf{r})\langle\mathbf{r}|\hat{H}^\alpha f_\beta(\varepsilon_F - \hat{H}^\alpha)|\mathbf{r}\rangle$$

$$= 2\sum_\alpha\sum_i f_\beta(\varepsilon_F - \varepsilon_i^\alpha)\langle\psi_i^\alpha|p^\alpha(\mathbf{r})|\psi_i^\alpha\rangle, \tag{16}$$

which leads to the approximate total energy

$$\tilde{E} = \tilde{\mathcal{E}} + Q[\tilde{\rho}] + \sum_{a,b} Z_a Z_b/R_{ab}, \tag{17}$$

where $Q[\tilde{\rho}]$ can be evaluated by three-dimensional integrations.

To summarize, the procedure to calculate $\tilde{\rho}(\mathbf{r})$ from a given $V_{\text{eff}}(\mathbf{r})$ is as follows: (i) Choose a partition function $p^\alpha(\mathbf{r})$ and a localized basis set $\{\phi_i^\alpha\}$ for each subsystem α; (ii) for each α, calculate the matrices $\mathbf{S}^\alpha$ and $\mathbf{H}^\alpha$ of Eq. (10) and then solve Eq. (12), which gives $\{\psi_i^\alpha, \varepsilon_i^\alpha\}$; (iii) determine ε_F by solving Eq. (14) and then $\tilde{\rho}(\mathbf{r})$ by Eq. (13). This procedure is coupled with Eq. (4) to achieve self-consistency. Finally, the total energy is given by Eq. (17). The new method has the following features.

(A) We employ a divide-and-conquer strategy. Not attempting the global approximation of the $N/2$ KS orbitals, we divide the electron density into contributions from subsystems using partition functions $p^\alpha(\mathbf{r})$ via Eq. (7), and then determine each contribution using local basis functions $\{\phi_i^\alpha\}$ via Eq. (8). It is conceptually appealing that the determination of the structure of a molecule can be based on its division into its constituent atoms, or chemical bonds, or functional groups, or fragments (examples of suitable partition functions will be given below). Computationally, the advantage of this approach is obvious: No construction nor diagonalization of the global Hamiltonian matrix is needed. Instead, diagonalization of the KS Hamiltonian for each subsystem as described in Eq. (12) can be carried out separately and concurrently, which is ideal for parallel processors. The coupling between each subsystem is minimal—only through the local potential and the value of ε_F.

(B) The KS theory is a limit of the present theory: In Eq. (8), if we let $\beta \to \infty$ and let $\hat{H}^\alpha$ be the same for all the subsystems, the usual LCAO KS Hamiltonian, for example, then the theory becomes the KS theory, independent of the choice of partition functions. This tells us that the localized basis set $\{\phi_i^\alpha\}$ for each α subsystem should at its (impractical) limit approach a complete set for the present theory to approach the KS theory. The partition functions should be designed to make Eq. (13) an accurate approximation to the density without going to this limit. Our numerical calculations below show our attempt in such design and its encouraging results.

The TF theory is another limit. Let the subsystem be points $\mathbf{r}_a$, $p^\alpha(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_a)$, and the summation over α become integration. Then represent the $\hat{H}^\alpha$, the Hamiltonian at point $\mathbf{r}_a$, by the local constant-potential approximation: $\hat{H}^\alpha = -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}_a)$. The eigenstates of such $\hat{H}^\alpha$ are plane waves and the present approach is reduced to the TF theory. This analysis puts the present method in a clear prospect: It presents a full spectrum of intermediate partitions of the systems between the global KS and the extremely local TF approaches. We also see that straightforward improvements of the TF theory would be to retain the point partition but to assume locally linear or quadratic approximations to $\hat{H}^\alpha$. The eigenstates of the three-dimensional linear and quadratic potentials are known and can be easily used in Eqs. (13)–(16).

(C) The present approximation for the KS eigenvalue sum $\tilde{\mathscr{E}}$ can be used in the non-self-consistent calculations proposed by Harris.[9] The resulting algorithm does not need the calculation of molecular density nor the global diagonalization of the KS Hamiltonian.

(D) Extension to the spin-polarized version of the theory is straightforward: Eqs. (13)–(16) apply to the corresponding spin components without the factor 2. Extension to describe fermions at finite temperature can also be made:[1,3] Let $1/\beta$ be the temperature, ε_F the chemical potential, and E_{xc} the exchange-correlation contribution to the free energy. Then the self-consistent solution gives the equilibrium fermion density. The approximation of Eq. (15) by Eq. (16) can be generalized to other properties, including the entropy:[3] That is,

$$\text{Tr}[g(\hat{H})] \cong \sum_\alpha \int d\mathbf{r}\, p^\alpha(\mathbf{r})\langle \mathbf{r}|g(\hat{H}^\alpha)|\mathbf{r}\rangle, \qquad (18)$$

where $g(x)$ is a general function.

(E) The present method, similar to the TF-type theory and unlike the conventional LCAO KS method, guarantees neither upper nor lower bound to the exact Kohn-Sham energy for a given $E_{\text{xc}}[\rho]$. But, a complete basis set (the same for all subsystems) used in the new method would produce the corresponding exact KS energy. The accuracy of the method is enhanced with the use of better basis functions, as will be shown in the example below.

We now demonstrate the proposed method with self-consistent calculations for the nitrogen diatomic system which we divide into two atomic subsystems. This is a simple yet very severe test, for the two subsystems are connected by a strong chemical bond.

To ensure the proper normalization, the partition function can conveniently take the form $p^\alpha(\mathbf{r}) = g^\alpha(\mathbf{r})/\sum_\alpha g^\alpha(\mathbf{r})$. We choose for the atomic subsystems $g^\alpha(\mathbf{r}) = [\rho_0^g(|\mathbf{r} - \mathbf{R}_a|)]^2$, where ρ_0^g is the spherical atomic electron density for the atom at $\mathbf{R}_a$. This is one of the forms of partition function used in multicenter three-dimensional integration for the LCAO KS approach.[10] The inverse temperature is set at $\beta = 50$ a.u., which corresponds to a temperature of 6300 K. The localized basis functions $\{\phi_i^\alpha\}$ are taken to be Slater-type atomic basis functions. Three sets of basis functions are used: single zeta, double zeta, and polarization, denoted by SZ, DZ, and P, respectively. The first two are from the Clementi-Roetti tables,[11] and one $3d$ and one $4f$ function are added to the quadruple zeta basis functions of the Clementi-Roetti table to form the polarization basis set. The exponents for the $3d$ and $4f$ functions are 2.5 and 2.0 for the nitrogen atom; their choice has been guided by that of McLean and Yoshimine.[12]

Other technical details are that all the multicenter three-dimensional integrations are carried out by the partition method of Delley,[10] with a scaled generalized Gauss-Laguerre quadrature rule for the radial coordinates;[13] the value of ε_F is obtained by a bisection method for solving Eq. (14); the electrostatic potential is calculated by the partition method of Delley;[10] the exchange-correlation energy functional used is the $X\alpha$ approxima-
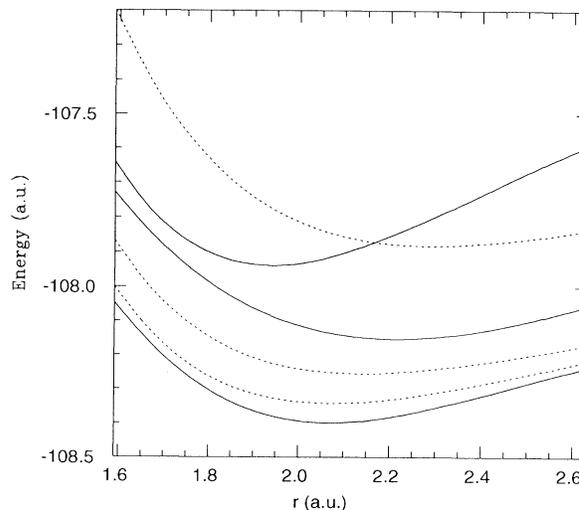

FIG. 1. Comparison of energies for N_2 between self-consistent calculations by the LCAO Kohn-Sham method (dashed lines) and by the present method (solid lines). The curves for both methods, from top to bottom, are, respectively, the results of SZ, DZ, and P basis sets.

TABLE I. Comparison of minimum energies (E_0) and bond lengths (r_0), in a.u., for N_2 molecule between LCAO Kohn-Sham approach and present work (PW), with three basis sets.

	P		DZ		SZ	
	(LCAO)	(PW)	(LCAO)	(PW)	(LCAO)	(PW)
E_0	−108.343	−108.400	−108.254	−108.153	−107.882	−107.940
r_0	2.075	2.069	2.136	2.215	2.288	1.940

tion, $E_{xc}[\rho] = -\frac{9}{8}\alpha(3/\pi)^{1/3}\int\rho^{4/3}\,d\mathbf{r}$, with $\alpha = 0.7$.

With the foregoing specification, we have carried out self-consistent calculations by the present method and also by the conventional LCAO Kohn-Sham method for comparison. Total energies versus bond lengths for the three basis sets are plotted in Fig. 1. The calculated minimum energies and equilibrium bond lengths are summarized in Table I. We note the following: (i) The present theory is capable of describing chemical bond formation; (ii) the accuracy of the present theory improves with the quality of the basis set; (iii) increasing β from 50 to 100 a.u. only changes the total energy at third or fourth digit after the decimal point. These calculations show the promise of the present theory. Its accuracy is much beyond the TF-type approaches.

The present theory allows a full spectrum of partitions of a molecule into subsystems. We expect its accuracy to increase with the size of subsystems. For subsystems more complex than atoms, the partition functions can be constructed by adding the partition functions of its constituent atoms, and the localized basis set can include atomic basis functions from its constituent atoms (and also from nearby atoms to accelerate convergence). The partition need not be exclusive—an atom may belong to more than one subsystem; for example, we can divide a molecule into all the bonded pairs of atoms. Whatever partition it may be, we hope that the present approach will enable the application of density-functional theory to large and complex molecules beyond the conventional approach.

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