Local Approximation of the Correlation Energy Functional in the Density Matrix Functional Theory

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A local approximation formula of the correlation energy functional E_c in terms of the first-order reduced density matrix (1-RDM) is presented. With the contracted Schrödinger equation the principal dependence of E_c on the natural occupation numbers n_i is identified. Using the effective mass theory, E_c is expressed as a functional of the local density and the local variable, $J = \sum_i \sqrt{n_i(1 - n_i)}\,|\varphi_i|^2$, where φ_i are the natural spin orbitals. This local approximation satisfies the homogeneous coordinate scaling relation, gives the exact result for a one-electron system, and is almost free from the exchange energy error. It reproduced about 90% of the correlation energies of atoms and molecules.

In this Letter we discuss the density matrix functional theory (DMFT), which is applicable to the ground state of atoms, molecules, and solids. These systems are often studied with the density functional theory (DFT), which uses the electron density as the basic variable [1]. The essential quantity in DFT is the exchange-correlation energy functional E_{xc}, which is mainly constructed with the local density approximation (LDA) [2] and the generalized gradient approximation (GGA) [3]. However, DFT has the inherent shortcomings that the systematic improvement of E_{xc} is difficult and that the exchange energy should also be approximated. Recently the exact exchange energy as a functional of density attracts primary attention, since it is believed that the approximated exchange energy contains larger error than the correlation energy [1].

It is well known that the first-order reduced density matrix γ (1-RDM) also serves as the basic variable of the ground state Ψ [4]. The n-RDM is defined as [5]

$$\Gamma^{(n)}(1' \cdots n', 1 \cdots n) = \frac{1}{n!}\langle \Psi | \phi^\dagger(1) \cdots \phi^\dagger(n) \\ \times \phi(n') \cdots \phi(1') | \Psi \rangle, \quad (1)$$

where $\phi^\dagger(\phi)$ and $i \equiv r_i \sigma_i$ denote the creation (annihilation) field operator and the set of the spatial and spin coordinates of an electron, respectively. The inherent advantage of DMFT is that the exact kinetic and exchange energies are known, and hence the correlation energy is the only unknown functional. DMFT becomes a promising alternative to DFT if a practical correlation energy functional is discovered. Among various interesting results [6–13], the remarkable success of the Goedecker-Umrigar (GU) functional [6] demonstrates the possibility of DMFT, and the previous power approximation [7] got renewed interest. Since then systematic methods to develop E_c have been anticipated.

The exchange and the correlation energies in DMFT are defined as [8]

$$E_x[\gamma] = -\frac{1}{2}\int \gamma(1,2)^2/r_{12}\,d1\,d2, \quad (2)$$

$$E_c[\gamma] = \min_{\Gamma^{(2)} \to \gamma} \int \Delta(12,12)/r_{12}\,d1\,d2, \quad (3)$$

where the correlated portion of 2-RDM is

$$\Delta(1'2', 12) = \Gamma^{(2)}(1'2', 12) \\ - \frac{1}{2}\{\gamma(1', 1)\gamma(2', 2) - \gamma(1', 2)\gamma(2', 1)\}. \quad (4)$$

The second term in the right-hand side of Eq. (4) is often expressed as the antisymmetric product, $-\gamma \wedge \gamma$. This $E_c[\gamma]$ satisfies simple relations [8] and thus has simpler structure than that of DFT. Some of these important relations are as follows: (i) the homogeneous coordinate scaling (HCS), $E_c[\gamma_\lambda] = \lambda E_c[\gamma]$, where the scaled 1-RDM is $\gamma_\lambda(r_1\sigma_1, r_2\sigma_2) = \lambda^3 \gamma(\lambda r_1\sigma_1, \lambda r_2\sigma_2)$, (ii) nonpositivity, $E_c \leq 0$, and (iii) zero correlation energy for an idempotent 1-RDM. Such constraints provide us with valuable guides to approximate the functional, since they severely restrict a possible form of E_c. However, our knowledge of $E_c[\gamma]$ at present is not enough to determine the functional without some assumptions.

A naive approximation of $E_c[\gamma]$ is to express it with electron density alone, $\rho(r) = \sum_\sigma \gamma(r\sigma, r\sigma)$. However, it does not work for the following reasons. (i) Since a Slater determinant can produce any reasonable density, variational minimization with this E_c gives the idempotent 1-RDM and the total energy below the true one. (ii) HCS requires that $E_c = C \int \rho^{4/3}\,dr$ where C is a constant, but it does not reproduce the correlation energy of the homogeneous electron gas (HEG). Thus a local approximation of $E_c[\gamma]$ or even the choice of variables for a local approximation is not a trivial problem.

We show that the functional is well expressed by the variable $J(r_1) = \sum_{\sigma_1}\int \gamma(1,2)^{1/2}\{\delta(2-1) - \gamma(2,1)\}^{1/2}\,d2$. This local approximation of E_c is proved to satisfy the three important conditions of the functional above. Numerical examination shows that it gives energies

better than the Hartree-Fock (HF) or LDA and comparable to the GGA for atoms and molecules.

Our approach is based on the contracted Schrödinger equation (CSE) [14],

$$\{v(r_1) - E\}\gamma(1', 1) +$$

$$2\int \{v(r_2) + 1/r_{12}\}\Gamma^{(2)}(1'2, 12)\, d2 +$$

$$3\int \Gamma^{(3)}(1'23, 123)/r_{23}\, d2\, d3 = 0, \quad (5)$$

where v is the one-body operator in the Hamiltonian. The RDMs of the exact eigenstate of H satisfy this equation. The 3-RDM in Eq. (5) is approximated as the sum of the following antisymmetric products [15–17]:

$$\Gamma^{(3)} = \gamma \wedge \gamma \wedge \gamma + 3\gamma \wedge \Delta + \dots. \quad (6)$$

By keeping the leading terms of Eqs. (5) and (6) and using the natural spin orbitals as the one-particle basis, the diagonal elements of the generalized Fock operator are approximated as [12]

$$\epsilon_i = \frac{2\alpha(2n_i - 1)}{n_i(1 - n_i)} \sum_{jkl} w_{ij}^{kl} \Delta_{ij}^{kl}. \quad (7)$$

Natural occupation numbers n_i and natural spin-orbitals φ_i are the eigenvalues and eigenfunctions of 1-RDM, respectively. The rescaling factor α is introduced to compensate the effect of the higher-order terms. This reconstruction leads to the first expression of E_c.

$$E_c = Tr(w\Delta) = \sum_i \frac{n_i(1 - n_i)\epsilon_i}{2\alpha(2n_i - 1)}. \quad (8)$$

Next we examine the dependence of this approximate E_c on n_i. Using the variational principle [9] of the ground-state energy, $\epsilon_i + \partial E_c/\partial n_i = \mu$, and by keeping only the leading terms of Eq. (8), we have the equation $2\alpha E_c = \sum_i n_i(1 - n_i)/(1 - 2n_i)\partial E_c/\partial n_i$. The solution of this partial differential equation which equals zero, as required, for an idempotent 1-RDM is

$$E_c = -\sum_i D_i\{n_i(1 - n_i)\}^{2\alpha}. \quad (9)$$

Equation (9) determines the principal dependence of E_c on n_i. The positive constants D_i are the functionals of the natural orbitals and the Coulomb interaction, and may weakly depend on the occupation numbers. Their coordinate scaling behavior is $D_i[\gamma_\lambda] = \lambda D_i[\gamma]$, since eigenvalues and eigenfunctions of γ_λ are n_i and $\lambda^{3/2}\varphi_i(\lambda r)$, respectively. If we neglect the orbital dependence and write $D_i = C\rho^{1/3}$, Eq. (9) for HEG can be written as

$$E_c = C \int \rho(r)^{1/3} J(r)\, d^3r, \quad (10)$$

$$J(r) = \sum_i \{n_i(1 - n_i)\}^{2\alpha} |\varphi_i(r)|^2. \quad (11)$$

The rescaling factor α must be $1/4$ to restore the correct result for small perturbation or the high-density limit of HEG [12]. Another choice of α is also proposed [10].

We evaluated E_c of Eqs. (8) and (10) for accurate RDMs. Those of HEG were taken from Refs. [18] and [19] for $0.1 \leq r_s \leq 1$ and $1 \leq r_s \leq 10$, respectively. RDMs of atoms and molecules were calculated by the quadratic configuration interaction with single and double substitutions (QCISD). The exact E_c were also estimated from these RDMs. Energy errors of QCISD with respect to the experimental values for two-, four-, and ten-electron systems in Table I were about 0.5, 5, and 20 mH, respectively.

As shown in Table I, Eq. (8) with $\alpha = 1/4$ reproduces E_c within the error percentage of 20% in these examples. Unfortunately, it cannot be used in the variational calculation unless the functional dependence of $\epsilon_i = \mu - \partial E_c/\partial n_i$ on 1-RDM is clarified. Keeping ϵ_i as the eigenvalues of the Fock operator in the variational calculation leads to the unphysical result of $E_c \rightarrow -\infty$ as $n_i \rightarrow 1/2$. Interestingly, the simple formula of Eq. (10) with $C = -1/4$ also gives rather good correlation energies. It reproduced about 90% of E_c for atoms and molecules, and about 99% and 124% for HEG of $r_s = 0.5$ and 3, respectively. The local variable $\rho^{1/3}J$ is a good measure of the local correlation energy.

Based on these observations, we propose the following local approximation of E_c. The system under consideration is divided into small subsystems. Each of them is regarded as HEG with the same local ρ and $\rho^{1/3}J$, or equivalently with the same ρ and J. Total correlation energy is the sum of E_c of each small subsystem, which is given by the correlation energy formula of HEG.

This local approximation requires us to express the electron mass m as a functional of ρ and J for the following reasons. (i) Gilbert's theorem indicates that the one-body operator of the Hamiltonian and hence the electron mass are the functionals of 1-RDM [4]. (ii) In order to satisfy HCS for HEG, m must be a functional of 1-RDM. Suppose γ is a ground-state 1-RDM of HEG described by the Hamiltonian,

$$H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m_e} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + v_N. \quad (12)$$

Then the scaled 1-RDM γ_λ becomes a ground-state 1-RDM of HEG with the electron mass of λm_e. Potential v_N stands for the electrostatic one from the neutralizing positive background. This coordinate scaling also changes the Wigner-Seitz radius $r_0 = (3/4\pi\rho)^{1/3}$ by the factor of λ^{-1}. Thus we have HCS, since dimensionless parameter $r_s = r_0(m_e e^2/\hbar^2)$ is invariant and E_c per electron is expressed as $E_c = (m_e e^4/\hbar^2)\epsilon(r_s)$.

Further development of the local approximation needs the correlation energy formula of HEG. The definition of E_c in DMFT is somewhat different from that in DFT, since the former involves the change of the kinetic energy t_c

TABLE I. Correlation energies evaluated for the accurate RDMs. Correlation energies are in mH while the numbers in parentheses are the percentage errors. RDMs of Refs. [18] and [19] for the electron gas and those of QCISD for atoms and molecules were also used to estimate the exact values. Errors of QCISD total energies with respect to the experimental energies were about 0.5, 5, and 20 mH for two-, four-, and ten-electron systems, respectively.

Method	Correlation energy in mH (error in %)												
	Electron gas				Atoms and molecules[a]								
	$r_s = 0.5$		$r_s = 3$		He		H_2		Be		B^+		Ne	
Eq. (8)	−162.7	(−19.1)	−72.2	(−6.2)	−95.8	(−7.2)	−101.2	(−11.5)	−246.3	(−17.5)	−305.2	(−21.8)	−733.7	(−0.2)
Eq. (10)	−134.7	(1.4)	−84.0	(−23.7)	−95.5	(−6.9)	−90.2	(0.6)	−195.2	(6.9)	−234.2	(6.5)	−663.9	(9.4)
Eq. (14)	−136.6	(0)	−67.9	(0)	−103.8	(−16.1)	−89.8	(1.1)	−212.2	(−1.2)	−256.9	(−2.5)	−794.8	(−8.5)
Estimated	−136.6	(0)	−67.9	(0)	−89.4	(0)	−90.8	(0)	−209.7	(0)	−250.6	(0)	−732.6	(0)

[a]Used are the uncontracted cc-pV5Z and cc-pVQZ Gaussian basis sets in Ref. [20] for atoms and molecules, respectively.

by the correlation and that of the exchange energy x_c. Using the virial theorem we express ϵ_c in DMFT as

$$\epsilon_c = \epsilon_{LDA} + \frac{d(r_s \epsilon_{LDA})}{dr_s} - x_c, \qquad (13)$$

where ϵ_{LDA} is the correlation energy of HEG [2] in DFT. Perturbation analysis shows that x_c and J/ρ are zero for $r_s \to 0$. We calculated x_c and J from the accurate 1-RDMs of HEG [18,19], and the results are fitted to the formulas, $x_c(r_s) = -e_2 r_s/(1 + e_1 r_s)$ and $J/\rho = J_1(r_s) = (d_2 r_s + d_3 r_s^2)/(1 + d_1 r_s)$, where $e_1 = 3.8954$, $e_2 = 5.2165 \times 10^{-2}$, $d_1 = 0.33980$, $d_2 = 1.0007$, and $d_3 = 3.1049 \times 10^{-2}$.

The correlation energy in our local approximation is

$$E_c = \int m\rho \epsilon_c(r_s) d^3r = \left(\frac{4\pi}{3}\right)^{1/3} \int \rho^{4/3} r_s \epsilon_c(r_s) d^3r,$$

$$r_s = J_1^{-1}(J/\rho), \qquad m = \left(\frac{4\pi\rho}{3}\right)^{1/3} r_s. \qquad (14)$$

The only difference of this functional from that of LDA is that the electron mass is expressed as a functional of ρ and J. However, this rather small difference solves the paradox of $E_c[\gamma]$ mentioned before. Equation (14) satisfies HCS. It also gives the exact result of $E_c = 0$ for a one-electron system or an idempotent 1-RDM, since r_s is zero. This new functional is almost free from the exchange energy error, since only the correlation contribution to the exchange energy is approximated.

In order to examine the validity of this approximation for inhomogeneous systems, we evaluated E_c of Eq. (14) for the accurate 1-RDMs of atoms and molecules. As shown in Table I, this approximation reproduced E_c of 99% to 116% in these examples. Note it involves only the local formula of the correlation energy. This result forms a contrast to that of LDA, which overestimates the correlation energy by a factor of 2. We also found that the average of the effective mass is about 0.4. This effective mass corrects the overestimation of LDA and is essential for the accurate description of an inhomogeneous system by the local approximation.

We also performed the self-consistent calculations for some atoms and molecules with this new functional. All the natural orbitals and the occupation numbers are variationally optimized within the N-representable range. The numbers of the spatial natural orbitals are 55 and 145 for He and NH_3, respectively. As shown in Table II, the present functional gives substantially better energies than HF or LDA. This result is impressive since it involves only the local formula of the correlation energy. Energies calculated by the present functional are slightly worse than those of GGA of PW91 or GU functional in these examples. Similar to LDA, this local approximation may also work well for simple metals.

The present functional gives rather large errors for two-electron systems. Possible reasons are as follows: (i) the exchange energy error. The approximated E_c of H_2 contains about 6×10^{-3} mH of exchange energy, which must be zero. Note, however, such exchange energy error is much smaller than in LDA. (ii) Orbital dependence of the constants D_i in Eq. (9). Generally these values are similar for the valence orbitals which mainly contribute to E_c. However, smaller values of D_i were observed for the orbitals with higher angular momentum in H_2. The assumption of the orbital independence may not be good for these systems.

In summary, we presented a systematic method to approximate $E_c[\gamma]$ by using the CSE. This study will replace the previous heuristic approach to construct the functional with a rigorous and more transparent one. Our ideas for approximation are to select two local variables which reflect electron-correlation effects, and to adopt the local approximation and the effective mass theory. Electron mass of HEG is varied in space to reproduce these local variables. CSE provides us a reliable way to select them. The simplest choice of ρ and J gives much superior total energies to LDA, and provides a good starting point for further improvement.

Extensions and refinements of the present functional may be achieved by the following methods. (i) Generalization to the spin-polarized system is easily established by taking ρ_α, ρ_β, and J as basic variables and by using the correlation energy formula of the polarized electron gas. Such theory is necessary for the correct description of bond dissociation. (ii) A better local variable may be obtained by making the constants

TABLE II. Total energies by the present functional of Eq. (14), Hartree-Fock, and the density functional methods. All the natural orbitals and occupation numbers were variationally optimized self-consistently.

System[a]	Total energy in Hartree (error in mH)								
	Hartree-Fock		LDA		GGA (PW91)		Present		Expt. [21]
He	−2.8616	(42.1)	−2.8721	(31.7)	−2.8999	(3.8)	−2.9324	(−28.7)	−2.9037
Be	−14.5730	(94.4)	−14.4471	(220)	−14.6478	(19.6)	−14.6913	(−23.9)	−14.6674
B$^+$	−24.2375	(111)	−24.0381	(311)	−24.3159	(33.0)	−24.3776	(−28.7)	−24.3489
Ne	−128.5468	(391)	−128.2326	(705)	−128.9457	(−8.1)	−128.9928	(−55.2)	−128.9376
F$^-$	−99.4593	(400)	−99.2662	(593)	−99.8788	(−20.0)	−99.9014	(−42.6)	−99.8588
H$_2$	−1.1335	(40.2)	−1.1374	(36.3)	−1.1705	(3.2)	−1.1913	(−17.6)	−1.1737
H$_2$O	−76.0647	(372)	−75.9082	(529)	−76.4414	(−4.2)	−76.4419	(−4.7)	−76.4372
NH$_3$	−56.2223	(341)	−56.1065	(457)	−56.5619	(1.1)	−56.5764	(−13.4)	−56.5630
F$_2$	−198.7516	(778)	−198.3382	(1191)	−199.5573	(−28.2)	−199.5550	(−25.9)	−199.5292
CO	−112.7889	(537)	−112.4743	(851)	−113.3256	(−0.2)	−113.3131	(12.3)	−113.3254

[a]Cc-pV5Z and cc-pVQZ basis sets in Ref. [20] for atoms and molecules, respectively. Diffuse functions are also included for F$^-$.

D_i in Eq. (9) orbital dependent. This dependence can be found by examining the results of HEG. (iii) The present functional does not satisfy the sum rule of the correlation hole exactly. The use of another variable, $I(r) = \sum_i n_i(1 - n_i)|\varphi(r)|^2$, eliminates this deficiency. This also makes it easier for the functional to satisfy the particle-hole symmetry, which is an example of the functional N representability [12]. Further studies about these issues are anticipated.

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