

## Correlation energy functional in the density-matrix functional theory

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A new systematic method is presented to construct a correlation energy functional in the density-matrix functional theory. A new exact relation, particle-hole symmetry, is presented, which states that the exact functional gives the same correlation energy for the first-order reduced density matrix (1-RDM) and the corresponding hole 1-RDM. Nakatsuji's density equations of the first and the second orders together with the decoupling approximation of the 3- and 4-RDMs are solved numerically to examine the properties of the correlation energy functional. This functional, defined as the solution of the set of equations, satisfies Levy's homogeneous coordinate scaling and the particle-hole symmetry and reproduces about 95% of the correlation energies of several molecules. By expanding these equations in perturbation series the leading term of the correlation energy functional is identified. Numerical analysis shows that this simplified functional, which contains one fitting parameter, reproduces the energies of several molecules accurately. The direction of further study is discussed.

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### I. INTRODUCTION

Density-matrix functional theory (DMFT), which uses the first-order reduced density matrix (1-RDM) as a basic variable instead of the electron density, could become a powerful and promising alternative to the conventional density functional theory (DFT) Ref. [1]. Density functional theory is now widely used to study the ground-state electronic structures of atoms, molecules, and solids, which share the same kinetic and electron-electron repulsion operators in the electronic Hamiltonians. The Hohenberg-Kohn theorem legitimizes the use of the electron density as a basic variable instead of the ground-state wave function for these systems. Similarly, the Hohenberg-Kohn-Gilbert (HKG) theorem states that under a given two-body interaction  $w$ , a ground-state 1-RDM determines the one-body potential  $v$  of the Hamiltonian and the wave function  $|\Psi\rangle$  of each state [2]. Hence the ground-state energy is a functional of the electron density or the 1-RDM, and the ground-state electron density or the 1-RDM is obtained by minimizing either of these energy functionals. The complexity of the description of the interacting electrons is masked by these functionals.

These functional theories replace the problem of interacting electrons with that of artificial noninteracting particles, by introducing the complicated functionals. In DFT, we have to express the kinetic, exchange, and correlation energies in terms of the electron density. However, the only unknown functional in DMFT is the correlation energy, since the kinetic and the exchange energies are expressed exactly in terms of the 1-RDM. This is the main advantage of DMFT over DFT in which the exchange energy attracts primary attention.

In DFT, electron density is obtained by filling the  $N$  lowest auxiliary orbitals called the Kohn-Sham (KS) orbitals, and we seldom calculate the electron density directly. In other words, DFT implicitly calculates the 1-RDM of the noninteracting system. This 1-RDM is often used as a basic variable when DFT is applied to a large system, since the RDM reflects the local nature of the system more directly than the

KS orbitals. Judging from these observations, DMFT, which uses the interacting 1-RDM as a basic variable, needs at most the same amount of computational effort as DFT, provided that the functional is evaluated as easily as that of the DFT.

The most important issue in DMFT at present is to construct practical correlation energy functionals. The discovery of such functionals would make DMFT a useful *ab initio* method for atoms, molecules, and solids. Unfortunately, few practical functionals are known today for the following reasons. (i) Little is known about the correlation energy functional itself, although several exact relations including Levy's homogeneous coordinate scaling were discovered [3]. (ii) No systematic methods are known to construct the correlation energy functional. In DFT, the local density approximation (LDA) and gradient expansion provide a systematic way to reach the exact functional.

In this paper, we report a new exact relation of the correlation energy functional called particle-hole symmetry. This symmetry states that the correlation energies of the 1-RDM and the corresponding 1-HRDM are always identical. Hence  $E_c$  should be a functional of the invariants under the particle-hole transformation.

Recently, Goedecker and Umrigar (GU) proposed a new energy functional in DMFT, which yields more accurate energies than the LDA and the generalized gradient approximation (GGA) in DFT for some atoms [4]. The GU functional is the first practical functional in DMFT, and their study demonstrated the potential power of DMFT. Some shortcomings of this functional are also pointed out [5,6].

In this paper, we propose a completely different approach to constructing a correlation energy functional. Our idea is to approximate  $E_c[\gamma]$  as well as the one-body operator  $v[\gamma]$  of the Hamiltonian. The HKG theorem states that the 1-RDM determines the wave function, since it determines the one-body operator of the Hamiltonian. Thus it is natural to examine the structure of this functional  $v[\gamma]$  and then the ground-state correlation energy of the reconstructed Hamiltonian. We used Nakatsuji's density equation [7,8], whose basic variable is the RDM instead of the wave function yet

which is equivalent to the Schrödinger equation. Approximation of the correlation energy functional is introduced as the decoupling of the higher-order RDMs in the equation. It is proved that the solution of this equation satisfies some known constraints on  $E_c$ , including the homogeneous coordinate scaling and particle-hole symmetry. The accuracy of this functional is examined by solving the equation numerically for some molecules. We found that the one-body operator  $v$  is reconstructed accurately and about 95% of the full-CI correlation energies are recovered. We simplified the equations by perturbation analysis and found that the numerical solutions of the simplified equations also reproduced the correlation energies well. All the converged 2-RDMs calculated as the by-products of  $E_c$  almost satisfied the important  $N$ -representability conditions. The equations proposed in this paper could be used as the basic equations to construct a correlation energy functional in DMFT.

The organization of this paper is as follows. In Sec. II, we review some known properties of the correlation energy functional and then derive a new exact relation, particle-hole symmetry. In Sec. III, we review the density equation briefly. Then we present a new set of equations to construct a correlation energy functional and discuss the mathematical properties of the solution. In Sec. IV, the accuracy of this functional is examined numerically for some molecules. Finally, the direction of further study is discussed.

## II. PROPERTIES OF THE CORRELATION ENERGY FUNCTIONAL

### A. Definition and some known properties

In this section we review some known properties of the correlation energy functional and then derive a new relation, particle-hole symmetry. The correlation energy functional  $E_c[\gamma]$  in DMFT is defined by Levy-Lieb-Valone's constrained search formula [9]

$$E_c[\gamma] = \min_{P \ni \Gamma^{(2)} \rightarrow \gamma} \int w(1,2) \{ \Gamma^{(2)}(1,2|1,2) - \gamma \wedge \gamma(1,2|1,2) \} d1 d2, \quad (1)$$

where  $w(1,2) = 1/r_{12}$  indicates the electron-electron repulsion operator. We denote the  $n$ -RDM  $n$ -hole RDM ( $n$ -HRDM), 1-RDM, and 1-HRDM as  $\Gamma^{(n)}$ ,  $\tilde{\Gamma}^{(n)}$ ,  $\gamma$ , and  $\tilde{\gamma}$ , respectively. The  $n$ -RDM and the  $n$ -HRDM are defined as

$$\Gamma^{(n)}(1' \dots n' | 1 \dots n) = \frac{1}{n!} \langle \Psi | \phi^\dagger(1) \dots \phi^\dagger(n) \phi(n') \dots \phi(1') | \Psi \rangle, \quad (2)$$

$$\tilde{\Gamma}^{(n)}(1' \dots n' | 1 \dots n) = \frac{1}{n!} \langle \Psi | \phi(1') \dots \phi(n') \phi^\dagger(n) \dots \phi^\dagger(1) | \Psi \rangle, \quad (3)$$

where  $\phi^\dagger$  and  $\phi$  are the creation and annihilation field operators, respectively, and  $i$  indicates the spatial and spin co-

ordinate of electron  $i$ . The wedge product of 1-RDMs in Eq. (1) expresses the independent-particle motion in the 2-RDM:

$$\gamma \wedge \gamma(1', 2' | 1, 2) = \frac{1}{2} \{ \gamma(1', 1) \gamma(2', 2) - \gamma(1', 2) \gamma(2', 1) \}.$$

Since the functional  $E_c$  is defined independently of the one-body potential, it is a universal functional and can be applied to any systems.  $P$  refers to the set of 2-RDMs derivable from fermion wave functions and ensembles, which is called the set of ensemble representable 2-RDMs or simply the set of representable 2-RDMs. In Eq. (1) the  $N$ -representable 2-RDM is found, which minimizes the electron-electron repulsion energy and at the same time reduces to the original 1-RDM. The second term subtracts the classical Coulomb and exchange energies. We cannot minimize the energy in Eq. (1) directly with respect to the 2-RDM because the necessary and sufficient conditions of the  $N$ -representability of RDMs are still unknown except for the 1-RDM [10]. The necessary and sufficient condition of the ensemble  $N$ -representability of the 1-RDM is that all the eigenvalues lie in the range from zero to one.

The correlation energy in DMFT is different from the exact non-relativistic energy minus the Hartree-Fock energy or the correlation energy in DFT. The exchange-correlation energy in DFT is defined as [1]

$$E_{xc}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + w | \Psi \rangle - \frac{1}{2} \int w(1,2) \rho(1) \rho(2) d1 d2 - T_s[\rho],$$

$$T_s[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle, \quad (4)$$

where  $|\Psi\rangle$ ,  $|\Phi\rangle$ , and  $\hat{T}$  indicate a general wave function, a Slater determinant, and the kinetic energy operator of electrons, respectively. The Kohn-Sham kinetic energy  $T_s$  gives the kinetic energy of the non-interacting system with the same electron density  $\rho$ . It approximates the true kinetic energy of the interacting system, and the difference is included in  $E_{xc}$ . The exchange energy in DFT is defined as

$$E_x[\rho] = - \frac{1}{2} \int w(1,2) |\gamma_{KS}(1,2)|^2 d1 d2,$$

where  $\gamma_{KS}$  is the Kohn-Sham 1-RDM of the non-interacting reference system. The energy difference  $E_{xc} - E_x$  gives the correlation energy in DFT which contains the kinetic energy contribution.

Let us summarize some known properties of the correlation energy in DMFT. Consider the Hamiltonian with a small coupling constant  $0 < \lambda \ll 1$

$$H = \frac{1}{\lambda} v + w = \frac{1}{\lambda} (v + \lambda w). \quad (5)$$

The ground-state 2-RDM of the Hamiltonian  $H$  is the same as that of  $\lambda H$  and the electron interaction  $\lambda w$  in  $\lambda H$  could be

treated as a perturbation. Diagrammatic analysis shows that for finite systems the leading term of the connected 2-RDM  $\Delta^{(2)} = \Gamma^{(2)} - \gamma \wedge \gamma$ , and hence  $E_c$  is proportional to  $\lambda$ :  $E_c \sim \lambda$ . In particular, the correlation energy is zero in the limit  $\lambda \rightarrow 0$  where the 1-RDM is idempotent. Levy proved that  $E_c = 0$  for any idempotent 1-RDMs  $\gamma_0$  [3].

This relation  $E_c[\gamma_0] = 0$  suggests the following approximation for  $E_c$ . The exact 1-RDM is often close to an idempotent 1-RDM for a molecule at an equilibrium geometry and one can choose  $\gamma_0$  so as to make  $\gamma - \gamma_0$  small. Since we know  $E_c[\gamma_0] = 0$ , the simple idea is to expand  $E_c$  about the idempotent 1-RDM:

$$E_c[\gamma] = \int (\gamma - \gamma_0) \frac{\delta E_c}{\delta \gamma}[\gamma_0] d1 d1' + \frac{1}{2} \int (\gamma - \gamma_0)^2 \frac{\delta^2 E_c}{\delta \gamma^2}[\gamma_0] d1 \dots d2' + \dots$$

Let us examine the functional derivative of the correlation energy called the correlation potential. The variational principle of the ground-state energy subject to normalization is

$$\frac{\delta E}{\delta \gamma} = \frac{1}{\lambda} v + j - k + \frac{\delta E_c}{\delta \gamma} = \mu, \quad (6)$$

where  $j$  and  $k$  are the Coulomb and the exchange operators defined as

$$j(1,2) - k(1,2) = \int w(2,3) \{ \delta(2-1) \gamma(3,3) - \gamma(1,3) \} d3. \quad (7)$$

Hence except for a constant  $\mu$ , the correlation potential is the reciprocal of the coupling constant  $\lambda$  for small enough  $\lambda$ . The correlation potential does not have a finite value for  $\lambda \rightarrow 0$  and the correlation energy functional does not have a Taylor expansion about the idempotent 1-RDM  $\gamma_0$ .

Another important relation of the correlation energy functional is Levy's homogeneous coordinate scaling [3]. The correlation energy of an 1-RDM  $\gamma$  and that of the dilated and normalized 1-RDM  $\gamma_\lambda$  have the simple relation

$$E_c[\gamma_\lambda] = \lambda E_c[\gamma]. \quad (8)$$

The dilated  $n$ -RDM is defined as

$$\begin{aligned} \Gamma_\lambda^{(n)}(1', \dots, n' | 1, \dots, n) \\ = \lambda^{3n} \Gamma^{(n)}(\lambda 1', \dots, \lambda n' | \lambda 1, \dots, \lambda n). \end{aligned} \quad (9)$$

The correlation energy in DFT shows a more complicated scaling relation:

$$\begin{aligned} E_c[\rho_\lambda] > E_c[\rho] \quad \lambda > 1, \\ E_c[\rho_\lambda] < E_c[\rho] \quad \lambda < 1. \end{aligned}$$

This is because  $\hat{T}$  and  $w$  have different degrees of homogeneity and the correlation energy in DFT also involves the kinetic energy contribution [1].

## B. Particle-hole symmetry of the correlation energy

In addition to these constraints, the correlation energy in DMFT satisfies a new exact relation, particle-hole symmetry. Valdemoro showed that the connected piece of the fermion 2-RDM and that of the 2-HRDM are identical [11]:

$$\Delta^{(2)} = \Gamma^{(2)} - \gamma \wedge \gamma = \tilde{\Gamma}^{(2)} - \tilde{\gamma} \wedge \tilde{\gamma}. \quad (10)$$

This equality is a direct consequence of antisymmetry with respect to exchange of fermions. By using this relation the 2-HRDM can be constructed from the 1- and 2-RDMs, since the 1-HRDM is given by  $\tilde{\gamma}(1',1) = \delta(1'-1) - \gamma(1',1)$ . Ruskai showed that every 2-HRDM satisfies the  $N$ -representability conditions of the 2-RDM and the set  $\mathcal{Q}$ , which has all the fermion 2-HRDMs, is the same as the set of  $N$ -representable 2-RDMs  $\mathcal{P}$  [12]. These two theorems and the definition of  $E_c$ , Eq. (1), result in the relation,

$$\begin{aligned} E_c[\gamma] &= \min_{P \ni \Gamma^{(2)} \rightarrow \gamma} \int w(1,2) (\Gamma^{(2)} - \gamma \wedge \gamma) d1 d2 \\ &= \min_{Q \ni \tilde{\Gamma}^{(2)} \rightarrow \tilde{\gamma}} \int w(1,2) (\tilde{\Gamma}^{(2)} - \tilde{\gamma} \wedge \tilde{\gamma}) d1 d2 = E_c[\delta - \gamma]. \end{aligned} \quad (11)$$

Here  $\delta$  is the unit matrix of rank  $\gamma$  [12]. The correlation energy functional must satisfy this fundamental symmetry  $E_c[\gamma] = E_c[\delta - \gamma]$ , irrespective of the detailed nature of the two-body interaction  $w$ . This relation is a consequence of the antisymmetry with respect to exchange of fermions. This particle-hole symmetry requires  $E_c[\gamma]$  to be a functional of the invariants under the particle-hole transformation, like  $\gamma(\delta - \gamma)$ . We also find that two ground states of the different systems, Hamiltonian  $v[\gamma] + w$  with  $\text{tr}(\gamma)$  electrons and Hamiltonian  $v[\delta - \gamma] + w$  with  $\text{tr}(\delta - \gamma)$  electrons have the same correlation energy.

Correlation energy in DFT does not satisfy this particle-hole symmetry since it also contains the correlation contribution of the kinetic energy. Since  $E_c$  in DMFT satisfies the strong constraints of the homogeneous coordinate scaling and the particle-hole symmetry while  $E_c$  in DFT does not, approximation of  $E_c$  in DMFT may be derived more easily than in DFT. Note that the electron density corresponds to the diagonal elements of the 1-RDM which are the only non-zero elements in the natural orbital basis.

## C. Goedecker-Umrigar functional

Recently, Goedecker and Umrigar (GU) reported that the diagonal elements of the 2-RDM  $\Gamma^{(2)}(1,2|1,2)$  can be approximated by

$$\begin{aligned} \Gamma^{(2)}(1',2'|1,2) \\ = \frac{1}{2} \{ \gamma(1'|1) \gamma(2'|2) - \gamma^{1/2}(1'|2) \gamma^{1/2}(2'|1) \} \\ - \frac{1}{2} \left\{ \sum_i n_i (n_i - \delta_{\sigma_1 \sigma_2}) \phi_i(1') \phi_i(2') \phi_i(2) \phi_i(1) \right\} \end{aligned} \quad (12)$$

in which  $n_i$  and  $\phi_i$  are the eigenvalues and eigenfunctions of the 1-RDM called the occupation numbers and the natural spin orbitals, respectively [4]. The second term on the right-hand side (rhs) represents the orbital self-interaction correction. Although Eq. (12) is rather simple the total energies of several atoms calculated from the 2-RDMs of Eq. (12) were more accurate than those of the LDA and the GGA in DFT [4]. Holas attributed this success to the fact that the first term on the rhs of Eq. (12) reduces to the original 1-RDM by the contraction [13]

$$(N-1)\gamma(1',1)=2\int\Gamma^{(2)}(1',2|1,2)d2, \quad (13)$$

where  $N$  is the total number of electrons. He also extended the GU functional to general powers other than  $1/2$ .

Although the GU functional showed remarkable success, some shortcomings are reported. Cioslowski and Pernal pointed out that the homogeneous electron gas of any density was predicted to be unstable by the original GU functional and they reported the acceptable range of the power [5]. Csanyi and Arias applied it to the homogeneous electron gas numerically and found that the results were significantly overcorrelated [6]. One also notices that it violates particle-hole symmetry and should contain powers of  $(\delta-\gamma)$  as well. The RDM functional in terms of the 1-RDM should be a functional of the two-body interaction  $w$  as well, since the HKG theorem holds under the fixed two-body interaction. Unfortunately, this dependence is hidden in Eq. (12) and it is difficult to inspect the physical pictures involved. Further studies about these issues are expected.

### III. NEW EQUATIONS FOR THE CORRELATION ENERGY FUNCTIONAL

The GU functional, which is the only practical functional so far reported, has several good properties, except for the instability of the homogeneous electron gas and the violation of particle-hole symmetry. One of the methods to obtain more accurate functionals is to correct these deficiencies of the functional. However, we discuss a completely different approach in this paper. The HKG theorem, which underlies the DMFT, states that the ground-state 1-RDM determines the one-body potential  $v$  of the Hamiltonian. Hence we examine first the structure of  $v[\gamma]$  and then the correlation energy  $E_c[\gamma]$  of the Hamiltonian  $v[\gamma]+w$ . To determine these functionals without using the wave function we use the density equation, which will be reviewed briefly. Next, a set of equations to determine  $v[\gamma]$  and  $E_c[\gamma]$  is presented. Mathematical properties of the correlation energy functional which is a solution of these equations are examined.

#### A. Density equation

The density equation, sometimes called the hierarchy or the contracted Schrödinger equation, determines the RDMs of the eigenfunction of the two-body Hamiltonian. The RDMs of the exact eigenstate of the Hamiltonian  $\hat{v}+w$  satisfy the  $n$ th-order density equation [7,8],

$$\begin{aligned} R^{(n)} &= -E\Gamma^{(n)} + \left\{ \sum_i^n \hat{v}(i) + \sum_{i>j}^n w(i,j) \right\} \Gamma^{(n)} \\ &+ (n+1) \int \left\{ \hat{v}(n+1) + \sum_i^n w(i,n+1) \right\} \\ &\times \Gamma^{(n+1)} d(n+1) + \binom{n+2}{2} \\ &\times \int w(n+1,n+2) \Gamma^{(n+2)} d(n+1) d(n+2) \\ &= 0, \end{aligned} \quad (14)$$

where  $\binom{n}{k}$  is the binomial coefficient. Nakatsuji's theorem states that in the domain of the  $N$ -representable RDMs the only exact  $(n+2)$ -RDM satisfies the  $n$ th-order density equation with  $n \geq 2$  [8]. Hence, without using the wave function, the exact RDMs could be obtained by solving this equation, subject to the sufficient  $N$ -representability conditions of the  $(n+2)$ -RDM. Unfortunately, the density equation itself is undetermined and it is not clear whether the limited  $N$ -representability conditions of the  $(n+2)$ -RDM known today are sufficient to determine the solution uniquely for general systems. Hence we previously took another route to solve the second-order equation by expressing the 3- and 4-RDMs in terms of the 1- and 2-RDMs. These RDMs are expressed symbolically:

$$\Gamma^{(2)} = \gamma \wedge \gamma + \Delta^{(2)}, \quad (15a)$$

$$\Gamma^{(3)} = \gamma \wedge \gamma \wedge \gamma + 3 \gamma \wedge \Delta^{(2)} + \Delta^{(3)}, \quad (15b)$$

$$\begin{aligned} \Gamma^{(4)} &= \gamma \wedge \gamma \wedge \gamma \wedge \gamma + 6 \gamma \wedge \gamma \wedge \Delta^{(2)} + 4 \gamma \wedge \Delta^{(3)} \\ &+ 3 \Delta^{(2)} \wedge \Delta^{(2)} + \Delta^{(4)}. \end{aligned} \quad (15c)$$

The wedge product  $\wedge$  generates the normalized antisymmetrized product [14]. The connected 3-RDM, the last term of Eq. (15b) is expressed as

$$\begin{aligned} \Delta^{(3)} &= \frac{1}{3!} \int \Delta^{(2)}(r'_1, r'_3 | q, r_3) P(q, q') \\ &\times \Delta^{(2)}(q', r'_2 | r_1, r_2) dq dq' + \dots, \end{aligned} \quad (16)$$

while  $P$  is defined for each idempotent 1-RDM  $\gamma_0$ :

$$\begin{aligned} P(q, q') &= P_0(q, q') \\ &- \int P(q, r') \{ \gamma(r', r) \\ &- \gamma_0(r', r) \} P_0(r, q') dr dr' \end{aligned} \quad (17)$$

where  $P_0(q, q') = 2\gamma_0(q, q') - \delta(q - q')$ . A convenient choice of  $\gamma_0$  is  $\gamma_0 = \theta(2\gamma - \delta)$ , where  $\theta$  is a step function. These relations were derived by the Green's function technique since the RDMs are the many-particle Green's functions whose time variables are equal to zero [15]. The second-order density equation was solved with various de-

coupling approximations of the 3- and 4-RDMs in terms of the 1- and 2-RDMs [14–16], and the results were quite satisfactory.

This density-equation approach could be applied to both the ground and excited states and to systems with any two-body interactions. The shortcoming is that the 4-RDM should be constructed at least implicitly and it requires more computational effort than DFT. Density functional theory or DMFT requires less computational demands and could be applied to larger systems.

### B. Reconstruction of the one-body operator

To obtain the equation for the correlation energy functional we first examine the one-body potential  $v$  in the Hamiltonian as a functional of the 1-RDM  $\gamma$ . The first-order density equation [Eq. (14) with  $n=1$ ] is used to reconstruct this one-body potential  $v[\gamma]$ . From the 1- 2-, and 3-RDMs, the equation

$$R^{(1)}(1'|1) + R^{(1)}(1|1') = 0 \quad (18)$$

determines  $v$  without a trivial constant  $C$ .  $R^{(1)}$  is invariant under the transformation  $v \rightarrow v + C$ , provided that the 1- and 2-RDMs satisfy the contraction relation Eq. (13). This non-uniqueness is consistent with the HKG theorem. Holas and March proposed a similar integral equation to calculate the exchange-correlation potential in DFT [17]. The 3-RDM in  $R^{(1)}$  is well approximated by Eqs. (15b) and (16) in terms of the 1-RDM  $\gamma$  and the connected piece of 2-RDM  $\Delta^{(2)}$ . If we include the first and the second terms in Eq. (15b) in the approximated 3-RDM, the diagonal elements of the generalized Fock operator in the natural orbital basis are

$$\epsilon_i = \frac{\alpha(1-2n_i)}{n_i(1-n_i)} \sum_{jkl} w_{ij}^{kl} \Delta_{ij}^{(2)kl}, \quad (19)$$

where  $n_i$  are occupation numbers of the natural orbitals and  $\alpha$  is an adjusting parameter.  $\alpha=1$  corresponds to the theoretical value. The generalized Fock operator is defined as

$$f(1,2) = v(1,2) + \int w(2,3) \{ \delta(2-1) \gamma(3,3) - \gamma(1,3) \} d3.$$

Equation (18) or (19) enables us to express the one-body operator or the Fock operator in terms of the 1- and 2-RDMs. Once the Hamiltonian is reconstructed the connected piece of the ground-state 2-RDM could be determined by various *ab initio* theories. Such self-consistent coupled equations define a correlation energy functional for each *ab initio* theory.

Although the idea is simple, the validity of the one-body operator functional  $v[\gamma]$  derived by Eq. (18) or (19) together with the decoupling approximation for the 3-RDM should be carefully investigated for the following reason. Our approximate formulas of RDMs work best for small coupling constant  $\lambda$  in the Hamiltonian of Eq. (5) since they are derived by perturbation theory. However, Eq. (6) indicates that  $v$  is almost reciprocal of  $\lambda$  in this regime and perturbation theory, which expands the quantities in the powers of  $\lambda$ , may lack enough accuracy. Thus numerical tests for typical systems

are essential to verify the applicability of these equations. In Sec. IV, we examine the accuracy of these equations numerically for some molecules.

### C. Determination of the connected 2-RDM

Equation (18) or (19) enables us to reconstruct the one-body operator  $v$  from  $\gamma$  and trial  $\Delta^{(2)}$ . Once we know the Hamiltonian, the connected piece of the ground-state 2-RDM  $\Delta^{(2)}$  is calculated by the equation

$$R^{(2)}(1',2'|1,2) + R^{(2)}(1,2|1',2') = 0, \quad (20)$$

which is equivalent to the second-order density equation. The 3- and 4-RDMs in  $R^{(2)}$  are approximated in terms of the 1-RDM and  $\Delta^{(2)}$  by Eqs. (15b), (15c), and (16). The correlation energy is given by the formula

$$E_c = \int w(1,2) \Delta^{(2)}(1,2|1,2) d1 d2. \quad (21)$$

Equations (18) and (20), with reconstruction formulas of the 3- and 4-RDMs, completely determine the  $v$ ,  $\Delta^{(2)}$  and  $E_c$  from a given 1-RDM  $\gamma$ . We refer the second-order functional to that solution with the approximate formulas of the 3- and 4-RDMs of Eqs. (15b) and (15c) in which the  $\Delta^{(4)}$  term is neglected. They contain the terms up to second order in  $\Delta^{(2)}$ . Approximation is introduced as the decoupling of the 3- and 4-RDMs which is closely related to coupled-cluster theory [15]. Although the connected 2-RDM could be determined by other *ab initio* theories, we use the density equation since it determines the 2-RDM without using the wave function and thus we can avoid the complexity of the wave function.

Equations (18) and (20), to obtain the correlation energy functional, can be applied to systems with any two-body interactions. Also, the underlying physical picture is clear and the approximation could be improved systematically. Characteristic properties of the Coulomb interaction, such as spherical symmetry, could be used to solve these equations to obtain an explicit formula for  $E_c$ . Note, this  $E_c$  is a universal functional of  $\gamma$  and we have to solve the equations only once to obtain the functional.

It is interesting that an approximate correlation energy functional could be constructed not only for the ground state but also for the excited states, although there is no theorem at present that establishes the 1-1 correspondence between the electron density (or the 1-RDM) and the wave function of the excited state. The density equations also hold for the excited states and density equation with the approximate  $N$ -representability condition, or the decoupling formula of the RDMs determined the RDMs of the excited states for a model system [14] and for a molecule [15].

Equations (18) and (20) make it possible to deduce the exact properties of  $E_c[\gamma]$  from the knowledge of RDMs as well as to derive the approximate formula for  $E_c$ . Perturbation expansion of these equations results in a perturbation series for the correlation energy functional. Clearly the exact reconstruction formulas of the 3- and 4-RDMs yield the exact functional.

Using natural orbital as the one-particle basis, Eq. (20) gives the following lowest-order contribution to  $\Delta^{(2)}$ :

$$\begin{aligned} & \Delta_{j_1 j_2}^{(2) i_1 i_2} \{ \epsilon_{j_1} (1 - 2n_{j_1}) + \epsilon_{j_2} (1 - 2n_{j_2}) \\ & \quad + \epsilon_{i_1} (1 - 2n_{i_1}) + \epsilon_{i_2} (1 - 2n_{i_2}) \} \\ & = \{ (1 - n_{j_1})(1 - n_{j_2})n_{i_1}n_{i_2} + (1 - n_{i_1})(1 - n_{i_2})n_{j_1}n_{j_2} \} \\ & \quad \times (w_{j_1 j_2}^{i_1 i_2} - w_{j_2 j_1}^{i_1 i_2}), \end{aligned} \quad (22)$$

where  $n_i$  are the occupation numbers of the natural orbitals and the orbital energies  $\epsilon_j$  are given by Eq. (19). We refer the lowest-order functional to the self-consistent solution of Eqs. (19) and (22). Solution of Eq. (22), which gives the leading term of  $E_c$ , looks like the lowest-order Moller-Plesset perturbation (MP) correction to the connected 2-RDM, since the occupation numbers are often close to zero or one. The remarkable difference of this lowest-order functional from the usual MP theory is that the orbital energies are expressed by the universal quantities of  $\gamma$  and  $w$  and hence the correlation energy becomes a universal functional. For the idempotent 1-RDM  $\Delta^{(2)}$  and  $E_c$  become zero, since the  $\epsilon_i$  in Eq. (19) diverge to  $\pm\infty$ .

#### D. Properties of the approximate functional

Next we discuss the mathematical properties of the second-order and lowest-order functionals. They are defined as the solution of Eqs. (18) and (20) with our second-order decoupling approximations of Eqs. (15b) and (15c) or the solution of Eqs. (19) and (22), respectively. We first examine Levy's homogeneous coordinate scaling [3]. If the approximate RDMs satisfy the correct scaling of Eq. (9) our functional should satisfy Eq. (8), since the decoupling of the 3- and 4-RDMs is the only approximation used. Hence we show that our approximate RDMs satisfy Eq. (9). In our decoupling approximation the unconnected piece is written as the simple product of lower-order RDMs. For example, the unconnected piece of the 3-RDM is the wedge product of  $\gamma \wedge \gamma \wedge \gamma$  or  $\gamma \wedge \Delta^{(2)}$ . Clearly these terms satisfy Eq. (9), provided that  $\gamma$  and  $\Gamma^{(2)}$  satisfy it. Connected 3-RDM of Eq. (16) contains two  $\Delta^{(2)}$  and the projector  $P$ , and they have a factor of  $\lambda^{6+6+3}$  in total. Integration with two internal spatial coordinates  $q$  and  $q'$  absorbs a factor of  $\lambda^{3+3}$  and the approximate  $\Delta^{(3)}$  also satisfies Eq. (9). Thus our approximate correlation energy satisfies the coordinate scaling relation.

Our correlation energy also satisfies particle-hole symmetry. Valdemoro showed that the connected  $n$ -RDM  $\Delta^{(n)}$  and connected  $n$ -HRDM  $\tilde{\Delta}^{(n)}$  are the same except for the sign [11]:

$$\tilde{\Delta}^{(n)} = (-1)^n \Delta^{(n)}. \quad (23)$$

The exact  $\Delta^{(n)}$  changes the sign of  $(-1)^n$  under the particle-hole transformation. Our approximate  $\Delta^{(3)}$  changes sign if we substitute the 1- and 2-RDMs with the corresponding HRDMs, since  $P$  changes sign while  $\Delta^{(2)}$  is invariant. Hence we have the relation  $E_c[\gamma] = E_c[\delta - \gamma]$ . Since the higher-

order connected RDMs derived by our method also satisfy the correct coordinate scaling and Valdemoro's relation, the systematic improvement is possible without violating these constraints.

## IV. NUMERICAL TESTS

### A. Reconstruction of the one-body operator

In this section we examine the equations to determine the correlation energy functional numerically. We first examine the accuracy of the reconstructed one-body operator of the Hamiltonian for some molecules. As we discussed in the previous section, a simple perturbation expansion may not be effective to approximate this functional, and numerical examinations are necessary to know the practical applicability of the equation for the reconstruction. Since this reconstructed Hamiltonian is used to calculate the connected 2-RDM and correlation energy, we compare those of the reconstructed Hamiltonian with those of the exact Hamiltonian.

Examples considered in this section are the ground states of molecules at experimental geometries [19] where the restricted Hartree-Fock method is a good approximation. STO-6G and double- $\zeta$  Gaussian-type atomic orbitals [18] are used as the basis sets, since full-CI is currently possible for this class of basis sets. Some 1s orbitals of the heavy atoms are fixed as the core orbitals. The ground-state exact 1-RDM  $\gamma_{\text{exact}}$  and correlation energy  $E_{c \text{ exact}}$  are calculated by the full-CI method. Then we compared  $E_{c \text{ exact}}$  with the approximate correlation energies which are calculated by the following procedures.

#### Second-order approximation

(1) Approximate the 2- and 3-RDMs from the full-CI 1-RDM  $\gamma_{\text{exact}}$ , and a trial connected 2-RDM  $\Delta^{(2)}$  by Eqs. (15a) and (15b). Solve the first-order density equation (18), to reconstruct the one-body operator  $v_{\text{approx}}$ .

(2) The ground-state  $\Delta^{(2)}$  of the reconstructed Hamiltonian  $H = v_{\text{approx}} + w$  is calculated by the full-CI method.

(3) These procedures are repeated until convergence. Equation (21) gives  $E_c$  from the converged  $\Delta^{(2)}$ .

#### Lowest-order approximation

(1) Approximate the Fock operator from  $\gamma_{\text{exact}}$  and a trial  $\Delta^{(2)}$  by Eq. (19). Subtract the Coulomb and the exchange operators of Eq. (7) from this Fock operator to calculate the one-body operator  $v_{\text{approx}}$ .

(2) The ground-state  $\Delta^{(2)}$  of the reconstructed Hamiltonian  $H = v_{\text{approx}} + w$  is calculated by the full-CI method.

(3) These procedures are repeated until convergence. Equation (21) gives  $E_c$  from the converged  $\Delta^{(2)}$ .

In both methods  $\Delta^{(2)}$  is rescaled so that the reconstructed 2-RDM satisfies the normalization condition of Eq. (13). The results are summarized in Tables I and II. Table I compares the results of the second-order approximation with those of the lowest-order one, while the first column of Table II shows the results of the lowest-order approximation applied to larger systems.

TABLE I. Energies and the errors of the connected 2-RDMs of the reconstructed Hamiltonian calculated by Eqs. (18) and (19). Numbers in square brackets indicate powers of 10.

Molecule orbitals <sup>a</sup>	Total energy (a.u.)			
	Second order Eq. (18)	First order Eq. (19)	SDCI	Full CI <sup>d</sup>
H <sub>2</sub> O	-75.7288	-75.7313	-75.7282	-75.7289
4×2	-120.845	-123.330	-117.196	-120.939
	7.80[-2]	-1.98	3.09	0
	2.20[-3]	4.23[-2]	7.29[-3]	0
NH <sub>3</sub>	-56.0549	-56.0568	-56.0532	-56.0549
4×3	-159.708	-161.665	-151.261	-159.779
	4.47[-2]	-1.18	5.33	0
	2.69[-3]	4.23[-2]	1.40[-2]	0
CH <sub>4</sub>	-40.1904	-40.1912	-40.1877	-40.1905
4×4	-196.001	-196.734	-181.908	-196.052
	2.58[-2]	-0.35	7.21	0
	1.81[-3]	1.37[-2]	2.12[-2]	0
N <sub>2</sub>	-108.6990	-108.7090	-108.6875	-108.7001
5×3	-329.882	-339.909	-281.029	-331.033
	0.35	-2.68	15.11	0
	9.99[-3]	6.84[-2]	8.25[-2]	0
CO	-112.4356	-112.4554	-112.4300	-112.4426
5×3	-295.467	-315.222	-253.982	-302.435
	2.30	-4.23	16.02	0
	2.44[-2]	5.98[-2]	7.80[-2]	0
C <sub>2</sub> H <sub>2</sub>	-76.7724	-76.7861	-76.7606	-76.7762
5×5	-389.971	-403.645	-324.605	-393.712
	0.95	-2.52	17.55	0
	2.06[-2]	5.49[-2]	1.03[-1]	0

<sup>a</sup>Number of occupied and empty orbitals in the active space.

<sup>b</sup>All the correlation energy errors are normalized to the full-CI correlation energies.

<sup>c</sup>Error of the connected 2-RDM measured by the Euclidean norm.

<sup>d</sup>Full-CI correlation energy of the exact Hamiltonian.

Since the connected 2-RDM has all the information about the two-body correlation, we examined the accuracy of the connected 2-RDM by the following two methods: correlation energy and the error of the connected 2-RDM measured by the Euclidean norm. As shown in Table I both the second and lowest-order approximations yielded correlation energies that agree quite well with the exact ones. The second-order approximation reproduced more than 99% of the correlation energies for the singly-bonded molecules and about 98% for the multiply-bonded molecules. The errors of the lowest-order approximation are somewhat greater but less than 2% of the correlation energies for singly-bonded molecules.

The definition of the correlation energy in DMFT is different from the usual one which is the energy difference between the Hartree-Fock and the full-CI methods. The SDCI correlation energy in this paper indicates

TABLE II. Energies and the errors of the connected 2-RDMs of the reconstructed Hamiltonian. Numbers in square brackets indicate powers of 10.

Molecule orbitals <sup>a</sup>	Total energy (a.u.)			
	Eq. (19)	Eqs. (19) and (22) <sup>e</sup>	SDCI	Full CI <sup>d</sup>
CH <sub>3</sub> F	-138.5340	-138.5027	-138.5249	-138.5300
7×4	-258.226	-226.878	-228.850	-254.230
	-1.57	10.76	9.98	0
	4.20[-2]	1.49[-1]	3.57[-2]	0
CH <sub>3</sub> OH	-114.7232	-114.6879	-114.7108	-114.7182
7×5	-313.177	-277.905	-272.246	-308.173
	-1.62	9.82	11.66	0
	5.72[-2]	1.63[-1]	4.52[-2]	0
CH <sub>3</sub> NH <sub>2</sub>	-95.0763	-95.0383	-95.0651	-95.0729
7×6	-325.921	-287.907	-284.167	-322.481
	-1.07	10.72	11.88	0
	1.01[-1]	1.54[-1]	4.49[-2]	0
C <sub>2</sub> H <sub>4</sub>	-77.9974	-77.9628	-77.9761	-77.9889
6×6	-401.281	-366.724	-377.319	-392.803
	-2.16	6.64	3.94	0
	4.83[-2]	3.00[-1]	2.77[-1]	0
CH <sub>2</sub> O	-113.5936	-113.5710	-113.5733	-113.5826
6×4	-345.599	-323.009	-293.716	-334.642
	-3.27	3.48	12.23	0
	7.06[-2]	2.61[-1]	6.08[-2]	0

<sup>a</sup>Number of occupied and empty orbitals in the active space.

<sup>b</sup>All the correlation energy errors are normalized to the full-CI correlation energies.

<sup>c</sup>Error of the connected 2-RDM measured by the Euclidean norm.

<sup>d</sup>Full-CI correlation energy of the exact Hamiltonian.

<sup>e</sup>Eqs. (19) and (22) with  $\alpha = 1/4$ .

$$E_{c \text{ SDCI}} = \int w \Delta_{\text{SDCI}}^{(2)},$$

where we refer  $\Delta_{\text{SDCI}}^{(2)}$  to the connected 2-RDM calculated from the SDCI wave function. Total energies other than SDCI are calculated from the 2-RDM  $\Gamma^{(2)} = \gamma_{\text{exact}} \wedge \gamma_{\text{exact}} + \Delta^{(2)}$  while those of SDCI are calculated from the 2-RDM  $\Gamma^{(2)} = \gamma_{\text{SDCI}} \wedge \gamma_{\text{SDCI}} + \Delta_{\text{SDCI}}^{(2)}$ . The results in Tables I and II indicate that the connected 2-RDMs of the reconstructed Hamiltonians calculated by the second- or lowest-order approximation are comparable to or more accurate than those of SDCI method. We conclude that the one-body operator in the Hamiltonian could be reconstructed accurately by Eq. (18) or (19) to calculate the connected 2-RDM or the correlation energy. Although the errors of  $\Delta_{\text{SDCI}}^{(2)}$  are sometimes larger than other approximated  $\Delta^{(2)}$ , the errors of the total energies are comparable, since the SDCI total energy is calculated from the connected 2-RDM and the 1-RDM of the SDCI wave function instead of the exact 1-RDM. Total en-

TABLE III. Correlation energies calculated by the various functionals and the SDCI method. Numbers in square brackets indicate powers of 10.

System orbitals <sup>b</sup>	Goedecker Umrigar	Present functional		SDCI	Full CI
		Second order	Lowest <sup>a</sup>		
	Total energy (a.u.)				
	Correlation energy ( $10^{-3}$ a.u.)				
	Correlation energy error <sup>c</sup> (%)				
	Error of the connected 2-RDM <sup>d</sup>				
F <sup>-</sup>	-99.4722	-99.5324	-99.5459	-99.5317	-99.5376
4 × 4	-188.078	-248.225	-261.796	-230.992	-253.420
	25.78	2.05	-3.31	8.85	0
	6.10[-1]	1.73[-2]	1.07[-1]	3.42[-2]	0
HF	-100.0899	-100.1409	-100.1553	-100.1413	-100.1470
4 × 6	-202.883	-253.945	-268.340	-237.720	-259.988
	21.96	2.32	-3.21	8.57	0
	6.15[-1]	2.01[-2]	1.14[-1]	3.25[-2]	0
H <sub>2</sub> O	-76.0928	-76.1340	-76.1520	-76.1353	-76.1423
4 × 8	-232.865	-274.081	-292.003	-253.717	-282.338
	17.52	2.92	-3.42	10.14	0
	6.94[-1]	2.86[-2]	1.44[-1]	4.24[-2]	0
NH <sub>3</sub>	-56.2654	-56.2956	-56.3086	-56.2972	-56.3043
4 × 10	-241.853	-272.077	-285.102	-250.421	-280.814
	13.87	3.11	-1.53	10.82	0
	7.36[-1]	2.99[-2]	1.53[-1]	4.52[-2]	0
CH <sub>4</sub>	-40.2760	-40.2917	-40.2971	-40.2941	-40.3001
4 × 12	-236.620	-252.297	-257.690	-233.597	-260.698
	9.24	3.22	1.15	10.40	0
	7.51[-1]	2.70[-2]	1.45[-1]	4.11[-2]	0
NH <sub>4</sub> <sup>+</sup>	-56.6222	-56.6490	-56.6628	-56.6514	-56.6582
4 × 12	-253.676	-280.409	-294.231	-259.952	-289.647
	12.42	3.19	-1.58	10.25	0
	7.25[-1]	2.48[-2]	1.46[-1]	4.05[-2]	0
BH <sub>4</sub> <sup>-</sup>	-27.0379	-27.0449	-27.0517	-27.0476	-27.0530
4 × 12	-215.557	-222.571	-229.331	-204.833	-230.714
	6.57	3.53	0.60	11.22	0
	7.88[-1]	3.30[-2]	1.48[-1]	4.53[-2]	0
N <sub>2</sub>	-109.0469	-109.0765	-109.1602	-109.0822	-109.1061
5 × 11	-415.386	-444.981	-528.643	-383.080	-474.541
	12.47	6.23	-11.40	19.27	0
	1.09	8.03[-2]	2.83[-1]	1.15[-1]	0

<sup>a</sup>Equations (19) and (22) with  $\alpha=1/4$ .

<sup>b</sup>Number of occupied and empty orbitals in the active space.

<sup>c</sup>All the correlation energy errors are normalized to the full-CI correlation energies.

<sup>d</sup>Error of the connected 2-RDM measured by the Euclidean norm.

ergies of the lowest-order functional are lower than the true energies while  $\Delta^{(2)}$  is well approximated.

### B. Connected 2-RDM and the correlation energy

Next we replace the full-CI to determine the connected 2-RDM in the iterative procedure with the second-order density equation of Eq. (20) or its lowest-order terms of Eq. (22). We showed previously that the second-order density equation with decoupling approximations of the 3- and

4-RDMs reproduced accurate correlation energies for atoms and molecules. Equation (22), which represents the lowest-order terms in this equation, yields the connected 2-RDM of the same accuracy as that of the first-order MP theory. The solution of the coupled equations (18) and (20) or (19) and (22) is calculated numerically for each full-CI 1-RDM. Approximate correlation energies  $E_c[\gamma_{\text{exact}}]$  are compared with the exact values and those of the GU functional which are summarized in Table III. The second column of Table II shows the results of the lowest-order approximation applied



TABLE IV. Reaction energies (kJ/mol) calculated by the lowest-order functional with  $\alpha=1/4$ . The total energy is minimized with respect to the occupation numbers, while the natural orbitals are fixed as those of the single and double configuration interaction (SDCI).

	$2\text{BH}_3$ $\rightarrow \text{B}_2\text{H}_6$	$\text{BH}_3 + \text{NH}_3$ $\rightarrow \text{BH}_3\text{NH}_3$	$\text{HF} + \text{F}^-$ $\rightarrow \text{FHF}^-$	$\text{C}_2\text{H}_4 + \text{HF}$ $\rightarrow \text{C}_2\text{H}_5\text{F}$
Hartree-Fock	52.8	94.2	219.7	76.4
Second-order Moller-Plesset	112.8	127.5	236.1	60.9
SDCI	102.8	122.8	227.1	69.0
Coupled-cluster doubles	106.9	125.3	226.2	57.7
Present	119.9	141.5	223.2	65.5
Density functional (B3LYP)	137.5	141.0	270.0	99.7
Experiment	156 <sup>a</sup>	130 <sup>b</sup>	176 <sup>c</sup>	38 <sup>d</sup>

<sup>a</sup>Reference [20].

<sup>b</sup>Estimated value, Ref. [21].

<sup>c</sup>Gas-phase value, Ref. [22].

<sup>d</sup>Estimated value, Ref. [23].

to larger systems. The correlation energy of the GU functional is calculated by the approximate 2-RDM of Eq. (12) from the full-CI 1-RDM, and the errors of the connected 2-RDMs measured by the Euclidean norm are also presented.

As shown in Table III, the results of the second-order functional agree quite well with the exact ones reproducing 94% ~ 98% of the correlation energies. Correlation energies and the errors of the connected 2-RDMs shown in Table III indicate that the approximate connected 2-RDMs are more accurate than those of SDCI method. The GU functional yields 75% ~ 93% of the correlation energies in our examples. Errors of the GU functional are larger but rather good, despite their simple structure.

The lowest-order functional also reproduces accurate correlation energies if the orbital energies in Eq. (19) are rescaled by a factor of 1/4. As shown in Tables II and III it reproduces about 90% ~ 110% of the correlation energies while it only gives half of the correlation energy without rescaling. The lowest-order functional tends to overestimate the correlation energies especially for triply-bonded molecules, while the connected 2-RDMs are more accurate than those of Eq. (12). It is surprising that the  $\Delta^{(2)}$  and the orbital energies  $\epsilon_j$  could be reconstructed accurately from the 1-RDM by the simple equations Eqs. (19) and (22) with only one parameter. We suggest these equations as the basic equations to develop a universal correlation energy functional.

The rescaling factor of the orbital energy could be rationalized by the following arguments.

(1) We split the correlation energy  $E_c$  into two parts. The first one is the energy difference between the Hartree-Fock and full-CI methods. We assume that it is approximated by the MP2 method. The MP2 energy correction is  $\text{tr}(w\Delta^{(2)})/2$ , where  $\Delta^{(2)}$  is the first-order connected 2-RDM calculated by MP theory. Solution of Eq. (22) approximates this first-order connected 2-RDM and hence the MP2 energy correction is half of the lowest-order correlation energy in DMFT.

(2) The second part of  $E_c$  is the difference between  $\text{tr}(v\gamma_{\text{exact}} + w\gamma_{\text{exact}} \wedge \gamma_{\text{exact}})$  and the Hartree-Fock energy. From the assumption in 1, this difference should be  $E_c/2$ . On the other hand, if the Hartree-Fock 1-RDM and the Fock

operator are approximated by  $\theta(2\gamma_{\text{exact}} - \delta)$  and Eq. (19), respectively, the energy difference is approximated by

$$\text{tr}\{f(\gamma_{\text{exact}} - \gamma_{\text{Hartree-Fock}})\} = 2\alpha E_c,$$

where  $\alpha$  is a scaling factor of the orbital energy. Thus approximately we have  $\alpha=1/4$ .

This scaling factor may partially compensate for some missing second-order terms.

We also examined the  $P$ ,  $Q$ , and  $G$  conditions of the  $N$  representability of the 2-RDM calculated by the present method and Eq. (12). Three matrices of  $P$ ,  $Q$ , and  $G$  in Ref. [10] must be non-negative for  $N$ -representable 2-RDMs. Sums of the negative eigenvalues of these matrices normalized to their traces are about  $5 \times 10^{-2}\%$  for the second-order functional, 0.1% for the lowest-order functional, and 5% for the 2-RDMs of Eq. (12). The 2-RDMs of Eq. (12) slightly violate these conditions. The contraction relation of Eq. (13) was well satisfied by the second-order method and 2-RDM of Eq. (12). The lowest-order method violates this condition, since  $\Delta^{(2)}$  of Eq. (22) gives a negligible contribution to the right-hand side of Eq. (13).

Finally, some chemical reaction energies are calculated by the lowest-order functional with rescaling factor  $\alpha=1/4$ . The results are summarized in Table IV. In these examples, molecular geometries are optimized by the coupled-cluster doubles (CCD) method and the double  $\zeta$  basis set is used. We minimize the total energy of the 1-RDM functional by changing the occupation numbers of the 1-RDM within the ensemble  $N$ -representable range, while the natural orbitals are fixed as the SDCI ones. The reaction energy in Table IV is the difference between the energy of the product and the sum of the energies of the reactant at large distance (10 Å). The reaction energies of DFT with the B3LYP functional and experimental values are also presented. The purpose of this calculation is to examine correlation effects on the reaction energies, but not to reproduce them within chemical accuracy since one needs at least a larger basis set and com-

plete geometry optimization. The examples also contain the three-center two-electron bond in diborane and the hydrogen bond in the  $\text{FHF}^-$  anion.

As shown in Table IV, electron correlations significantly change the reaction energies of  $2\text{BH}_3 \rightarrow \text{B}_2\text{H}_6$  and  $\text{BH}_3 + \text{NH}_3 \rightarrow \text{BH}_3\text{NH}_3$ . Our functional corrects the energies of the restricted Hartree-Fock (RHF) method to those of more accurate methods like DFT of the B3LYP functional, SDCI, and CCD. Density functional theory yielded somewhat different energies from other correlated methods. One of the reasons is that DFT is designed to reproduce the experimental energies rather than the full-CI energies of the finite basis set. Although we do not apply this method to open-shell systems because of program limitations, it could be extended to such systems by utilizing the unrestricted scheme or the multi-reference formulation of the RDMs [24].

The purpose of this paper is to establish the reliability of Eqs. (18) and (20) or Eqs. (19) and (22) as the basic equations to construct a correlation energy functional. In this paper, the values of the functional were calculated by a self-consistent solution of coupled equations and the actual calculation of  $E_c$  requires the same amount of effort as the conventional many-body methods. Since this functional is universal and we only have to solve it only once in principle, the explicit formula of the solution is of great importance and the approximate universal functional could be derived by solving the equations for some special systems or for some model 1-RDMs. Further studies about this issue are expected.

## V. SUMMARY

To construct a correlation energy functional  $E_c$  in density matrix functional theory, we reported a new exact relation

for  $E_c$  called the particle-hole symmetry and a set of equations to determine  $E_c$ . Particle-hole symmetry indicates that the correlation energies are the same for the 1-RDM and corresponding 1-HRDM, and that  $E_c$  is a functional of the invariants under particle-hole transformation. Equations of  $E_c$  are derived from the first- and second-order density equations together with the decoupling approximations for the 3- and 4-RDMs. It is proved that the solution of these equations satisfies the conditions of  $E_c$ , the homogeneous coordinate scaling and particle-hole symmetry. Solutions of these equations are calculated numerically from the full-CI 1-RDMs of molecules and the calculated correlation energies are compared with the full-CI ones. The present equations reproduce about 95% of the correlation energies for several molecules. The leading term of the equations with only one parameter reproduces the energies of several molecules and chemical reaction energies accurately. Connected 2-RDMs almost satisfy the important  $N$ -representability conditions of the  $P$ ,  $Q$ , and  $G$  conditions. The set of the equations presented here could be used as the basic equation to develop the correlation energy functional, and the solutions of some special systems give us valuable information about the functional.

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- [1] W. Kohn and L.J. Sham, *Phys. Rev. A* **1133**, 140 (1965); R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989); E. K. U. Gross and R. M. Dreizler, *Density Functional Theory* (Plenum, New York, 1995).
- [2] P. Hohenberg and W. Kohn, *Phys. Rev. B* **864**, 136 (1965); T.L. Gilbert *ibid.* **12**, 2111 (1975).
- [3] M. Levy, in *Density Matrices and Density Functionals*, edited by E. Erdahl and V.H. Smith, Jr. (Reidel, Dordrecht, 1987); R.A. Donnelly and R.G. Parr, *J. Chem. Phys.* **69**, 4431 (1978).
- [4] S. Goedecker and C.J. Umrigar, *Phys. Rev. Lett.* **81**, 866 (1998).
- [5] J. Cioslowski and K. Pernal, *J. Chem. Phys.* **111**, 3396 (1999).
- [6] G. Csanyi and T.A. Arias, *Phys. Rev. B* **61**, 7348 (2000).
- [7] L. Cohen and C. Frishberg, *Phys. Rev. A* **13**, 927 (1976).
- [8] H. Nakatsuji, *Phys. Rev. A* **14**, 41 (1976).
- [9] M. Levy, *J. Chem. Phys.* **67**, 724 (1977); S.M. Valone, *ibid.* **73**, 1344 (1980); E.H. Lieb, *Int. J. Quantum Chem.* **24**, 243 (1983).
- [10] A.J. Coleman, *Rev. Mod. Phys.* **35**, 668 (1963); C. Garrod and J. Percus, *J. Math. Phys.* **5**, 1756 (1964); H. Kummer, *ibid.* **8**, 2063 (1967); R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960); W.B. McRae and E.R. Davidson, *J. Math. Phys.* **13**, 1527 (1972); E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976); E.R. Davidson, *Chem. Phys. Lett.* **246**, 2009 (1995).
- [11] C. Valdemoro, *Phys. Rev. A* **45**, 4462 (1992); F. Colmenero and C. Valdemoro, *ibid.* **47**, 979 (1993).
- [12] M.B. Ruskai, *J. Math. Phys.* **11**, 3218 (1970).
- [13] A. Holas, *Phys. Rev. A* **59**, 3454 (1999).
- [14] D.A. Mazziotti, *Phys. Rev. A* **57**, 4219 (1998); *Chem. Phys. Lett.* **289**, 419 (1998); *Phys. Rev. A* **60**, 3618 (1999).
- [15] H. Nakatsuji and K. Yasuda, *Phys. Rev. Lett.* **76**, 1039 (1996); K. Yasuda and H. Nakatsuji, *Phys. Rev. A* **56**, 2648 (1997); K. Yasuda, *ibid.* **59**, 4133 (1999).
- [16] F. Colmenero and C. Valdemoro, *Int. J. Quantum Chem.* **51**, 369 (1994); C. Valdemoro, L.M. Tel, and E. Pérez-Romero, *Adv. Quantum Chem.* **28**, 33 (1997).
- [17] A. Holas and N.H. March, *Int. J. Quantum Chem.* **61**, 263 (1997).
- [18] E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 428 (1974); T.H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970).

- [19] L. E. Sutton, D. G. Jenkin, and A. D. Mitchell, *Tables of Interatomic Distances* (Chemical Society, London, 1958).
- [20] B. Rušćić, C.A. Mayhew, and J. Berkowitz, *J. Chem. Phys.* **88**, 5580 (1988).
- [21] A. Haaland, *Angew. Chem. Int. Ed. Engl.* **28**, 992 (1989).
- [22] H. Keller-Rudek, P. Kuhn, H. List, P. Merlet, S. Ruprecht, H. Vanecek, and J. Wagner, *Gmelin Handbook of Inorganic Chemistry Fluorine, Supplement Volume 3, Compounds with Hydrogen* (Springer-Verlag, New York, 1982).
- [23] S. Kato and K. Morokuma, *J. Chem. Phys.* **73**, 3900 (1980).
- [24] W. Kutzelnigg and D. Mukherjee, *J. Chem. Phys.* **107**, 432 (1997).