Multireference Density Functional Theory With Orbital-Dependent Correlation Corrections

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ABSTRACT: The features of ab initio wave function-driven multireference (MR)-density functional theory (DFT) approach based on the partially interacting reference system for ground and excited states are discussed from the viewpoint of a simple classification of electron correlation effects. Our previous MR-DFT approach covers (i) structure-free, and (ii) resonating-type correlations, but does not include (iii) orbital-dependent correlation effects. Indeed, the computational results of excitation energies of atoms imply that the state-dependent correlations remain if the CASCI wave functions are used for the wave function part of MR-DFT and semilocal correlation functional is used. Thus, we present an orbital-dependent residual correlation for complete active space (CAS) DFT to describe type (iii) of correlation effects.   © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 3312–3324, 2006

Key words: multireference density functional theory; excited states; complete active space perturbation theory; orbital-dependent correlation

Introduction

In the Kohn–Sham (KS) density functional theory (DFT), a complicated many-body problem is converted into a mean-field problem by introduc-

ing noninteracting reference system, without approximating on the total energy functional, but with changing its partition [1, 2]. All nonclassical electron interaction effects are covered by an exchange-correlation (XC) term, for which a semilocal density functional approximation is usually employed. This formalism enables us to treat large molecules for which wave function theory cannot be applied, and KS-DFT has become a popular tool in computational chemistry. However, two types of

problems remain. First, the mean-field treatment leads to unsatisfactory results for systems that have strong multireference (MR) characters. In restricted KS-DFT, electron correlations of the double excitation type are not included explicitly. A practical approach to covering these effects, i.e., the spin-unrestricted KS-DFT, leads to symmetry-broken solutions, encountering so-called symmetry-dilemma problem [3–8]. The electronic correlation dominated by the low-lying configurations is known as a "static correlation" in the field of quantum chemistry. It remains unclear whether the difficulties of dealing static correlation with KS-DFT might be related to practice, rather to than principle, in case calculations using a modest basis set. The problem could be resolved by improving the XC functional on a real space basis, as any N-representable density can be yielded by a single-determinant reference wave function in real space [2]. But up to now, any XC functional for the spin symmetry-adapted KS-DFT method, by which we can describe the static correlation correctly, has remained unknown. Instead, a straightforward remedy for the case is to introduce the MR wave function into the DFT [9–47]. (The CI-DFT equation presented in Ref. [44], however, was derived under the assumption that the effective CI-DFT solution corresponds to a stationary point of energy expectation value of the effective CI-DFT Hamiltonian, but this does not hold for most cases of CI-DFT: the relation between RC functional and its potential for CI equation in this reference is corrected to Eq. (9) in the text.)

A second problem in applications of KS-DFT for chemical systems arises from the semilocal approximation for the XC functional such as local density approximation (LDA) and general gradient approximation (GGA), although the LDA XC functional is nearly exact for a homogeneous electron gas. One reason is that a potential of a molecular system has some structure, which is far from a flat and homogeneous field. The term "structure" here is used not only in the sense that a molecule has a symmetry such as a point group, but also in the general sense to denote all inhomogeneous features of a molecule. Electrons in molecules are bound in almost all systems, and thus are dominated by the structure of the molecular system and molecular orbitals. Such is critically different to itinerant electrons in solids. This may cause that LDA (and GGA) succeeds in metal and needs further improvement in molecules. The self-interaction error, which often causes a serious problem in chemical applications such as spurious overbinding of weak molecular interactions or missing reaction barriers, is also related to the semilocal approximation of the XC functional. Since the classical Coulomb hole and the exact exchange hole of a one-electron system do not depend on the position of the reference electron, but on the structure of the system, a nonlocal approximation, such as the self-interaction correction (SIC) and exact exchange functional, is required to avoid SIE [48]. A detailed electronic structure, such as shell structure, is reproduced by introducing an exact exchange functional [49]. If we recall that the MR characters of low-lying configurations can always be converted into the resonating valence bond (VB) pictures [50], and that possible VB components of resonating states are determined by a given molecular geometry [51], the structure of molecule becomes an origin of the strong MR characters of molecules in some cases such as ion-radical systems. It is noteworthy that the electrons in so-called strongly correlated systems are also bound at sites, and are affected strongly by the direction of neighbor sites, i.e., the structure of the system and the atomic orbitals that they occupy. In fact, LDA fails to describe the insulating antiferromagnetic states of the $3d$ transition metal monoxides, MnO, NiO, while the orbital-dependent SIC-LDA [48] and optimized effective potential (OEP) method [52] lead to the correct bandgaps. In almost all explicit XC functionals, explicit information of the direction from a reference electron to correlated electrons is lost when the spherical average of the XC hole is taken. All of this amounts to saying that there is a significant difference between electron correlations of homogeneous electron gas and those of molecular or strongly correlated systems.

For simplicity, we classify electron correlations into three types denoted (i), (ii), and (iii) in Figure 1(a) based on the above discussion. Correlations of the homogeneous electron gas system or similar systems such as a metallic state of solid are of the structure-free type (i). The KS-DFT with LDA/GGA works well for these systems. However, the resonating type (ii) of correlations becomes essential to explain the electronic properties of chemical compounds [51]. It is well described by an appropriate MR wave function consisting of low-lying configurations. Another is orbital-dependent correlations (iii), described as virtual excitation processes of electrons among orbitals. These three types of correlations overlap. It is noteworthy that one of corresponding method could cover other regions when the approximation is improved. It is known that the CI method with an infinite basis set, i.e., a full CI limit, covers all electron correlations. The
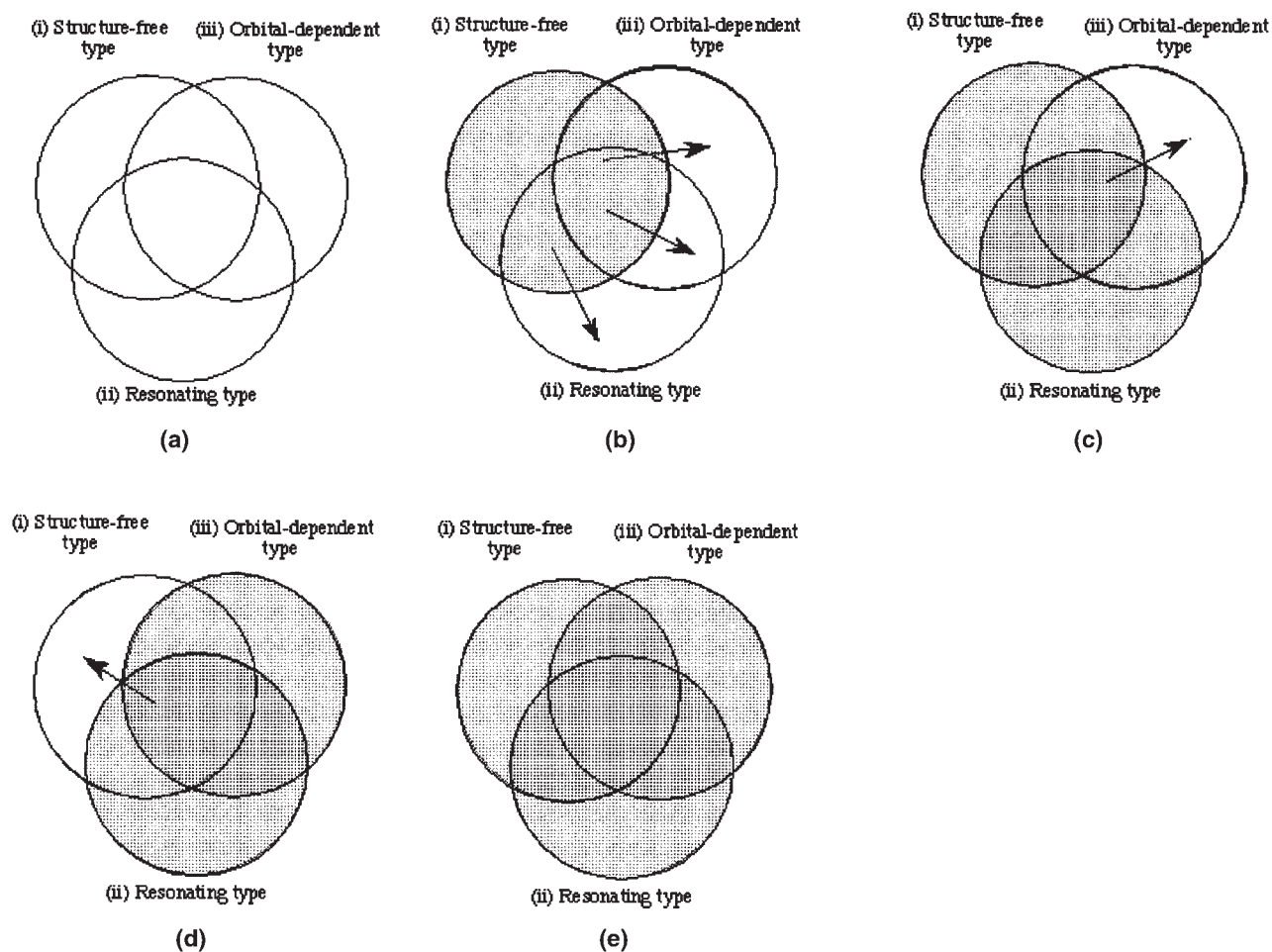
FIGURE 1. Classification of electron correlations and the regions covered by several classes of electronic structure theories. (a) Three types of electron correlations. (b) Region covered by KS-DFT. (c) Region covered by MR-DFT using semilocal correlation correction. (d) Region covered by MR-DFT using orbital-dependent correction. (e) Region covered by an ideal method combining CI, PT, and DFT approaches.

situation is same for the infinite-order MBPT, as far as the perturbation expansion is converged. It might be possible by improving a usual XC functional in KS-DFT to cover type (ii) and (iii) correlations, as shown in Figure 1(b). However, it is easier to describe type (ii) by CI, and type (iii) by MBPT or by using the orbital-dependent xc terms [48, 49, 52–62], respectively.

Two new directions i.e., MR-DFT [9–47] and KS-DFT with the OEP method [48, 49, 52–62] in DFT are developed for these purposes. MR-DFT using the Coulomb division method [27, 29–38, 45, 46] can be applied for any combination of wave function and DFT xc functional. Indeed, an MBPT-DFT approach has been developed and successfully applied for the weak molecular interaction problem

(see Ref. [39]). In contrast, a "wave function-driven" type MR-DFT, employing a modest CI including only low-lying configurations, is obviously designed to cover the shaded region, i.e., (i) and (ii) correlations, as described in Figure 1(c).

In the present work, we begin with this type of MR-DFT for both ground and excited states by employing a usual semilocal correlation functional. We present a simple approach of this type MR-DFT. However, our MR-DFT approach overestimated the excitation spectrum of atoms, as shown below. Thus, we propose a simple orbital-dependent correction within the MR-DFT framework. The relationship between this orbital-dependent type MR-DFT to KS-OEP and MR-WFT is discussed.

MR-DFT for the Ground State: Iterative CI-DFT

We begin with a brief summary of MR-DFT for the ground state. The starting point is the ground-state energy for the system under the external potential $V_{\text{ext}}(\mathbf{r})$:

$$E_0 = \text{Min}_{\rho(\mathbf{r}) \to N} E[\rho(\mathbf{r})]$$

$$= \text{Min}_{\rho(\mathbf{r}) \to N}\{F[\rho(\mathbf{r})]$$

$$+ \int d\mathbf{r}\rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})\}, \quad (1)$$

using the Hohenberg–Kohn–Levy universal functional [63, 64]:

$$F[\rho(\mathbf{r})] = \text{Min}_{\Psi \to \rho(\mathbf{r})}\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle. \quad (2)$$

Introducing the noninteracting reference system, $F[\rho(\mathbf{r})]$ then has the form of the KS division [1]:

$$F[\rho(\mathbf{r})] = \text{Min}_{\Phi \to \rho(\mathbf{r})}\langle\Phi|\hat{T}|\Phi\rangle + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ E_{\text{XC}}[\rho(\mathbf{r})]. \quad (3)$$

By contrast, MR-DFT methods produce different types of partition based on partially interacted systems [27, 29–38, 46]:

$$F[\rho(\mathbf{r})] = \text{Min}_{\Psi \to \rho(\mathbf{r})}\langle\Psi|\hat{T} + \hat{V}_{ee}^p|\Psi\rangle + U_{\text{RCC}}^p[\rho(\mathbf{r})]$$

$$+ E_{\text{RXC}}^p[\rho(\mathbf{r})], \quad (4)$$

or

$$F[\rho(\mathbf{r})] = \text{Min}_{\Psi \to \rho(\mathbf{r})}^p\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle + E_{\text{RC}}^p[\rho(\mathbf{r})]$$

$$= F^p[\rho(\mathbf{r})] + E_{\text{RC}}^p[\rho(\mathbf{r})]. \quad (5)$$

In Eq. (4), the electron repulsion operator, $\hat{V}_{ee}^p$ is incorporated into the universal functional, and the remaining terms at the right side are residual classical Coulomb (RCC) and residual exchange-correlation (RXC) terms, respectively. Savin and coworkers developed this "Coulomb-driven" MR-DFT by employing various screened Coulomb operators, such as the Yukawa potential [27], the attenuated Coulomb potential using the error function [30, 31], and the erfgau function [34, 35], for $\hat{V}_{ee}^p$. An impor-

tant aspect of this MR-DFT is that a screened parameter interconnects between the KS-DFT and the exact WFT limits, providing a practical tool for the adiabatic connection approach of DFT.

In contrast, a practical MR-DFT computational scheme is based on the modified universal functional $F^p[\rho(\mathbf{r})]$ of "wave function-driven" MR-DFT [9–26, 28, 40–47] given in Eq. (5): $F^p[\rho(\mathbf{r})]$ is defined by limiting a variational space to a specific extent of a wave function expansion. We follow this type of MR-DFT throughout this study.

From the definition, $F^p[\rho(\mathbf{r})]$ is bounded below by $F[\rho(\mathbf{r})]$, and the difference between these two terms provides just the residual correlation (RC) functional, $E_{\text{RC}}^p[\rho(\mathbf{r})] \equiv F[\rho(\mathbf{r})] - F^p[\rho(\mathbf{r})]$ that is always negative. Thus, an alternative representation of the ground-state energy:

$$E_0 = \text{Min}_{\rho(\mathbf{r}) \to N}\{F^p[\rho(\mathbf{r})] + \int d\mathbf{r}\rho(\mathbf{r})V_{\text{ext}}(\mathbf{r}) + E_{\text{RC}}^p[\rho(\mathbf{r})]\},$$

$$(6)$$

becomes valid by virtue of the original Hohenberg–Kohn theorem. The Euler equation of MR-DFT is given by

$$\frac{\delta F^p[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = -\left\{V_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{RC}}^p[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}\right\} + \mu. \quad (7)$$

As we are now working on a partially interacting system, we have to solve the effective many-body equation,

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}} + \hat{V}_{\text{RC}})|\Psi\rangle = E_{\text{MR-DFT}}|\Psi\rangle, \quad (8)$$

instead of the KS equation. Here $\hat{V}_{\text{RC}}$ is the RC potential corresponding to RC functional that depends on density. As the RC potential is evaluated using the CI solution itself, Eq. (8) must be solved by iteration. Thus, this equation is called "iterative CI-DFT." The extension from ICI-DFT to multiconfiguration self-consistent field (MCSCF)-DFT is straightforward [24, 25, 44].

One may note that, although it is assumed throughout this work, that the "wave function-driven" MR-DFT is based on the CI method, in principle it could be implemented in quantum Monte Carlo (QMC) computations such as variational MC (VMC) and diffusion MC (DMC) methods [65]. For the sake of completeness, we shall touch a possible scheme for QMC-DFT. In the

QMC-DFT approach, $F^p[\rho(\mathbf{r})]$ is determined within a simple Jastrow factor (VMC) or a given fixed node (DMC) [21], and the remaining degree of freedom to yield the exact wave function is covered by an RC potential. As for an RC functional in QMC-DFT, it is possible to use a Colle–Salvetti type of a correlation functional [21], by which electron correlation effects beyond the reference wave function Ψ is included in the correlation functional.

We would like to pause here to consider the relation between the RC term and its corresponding potential in detail. A variation up to first order with Eq. (8) leads to the relation, $\langle\Psi|\delta\hat{V}_{RC}|\Psi\rangle = \delta E_{MR\text{-}DFT}$. Here if we assume that $E_{MR\text{-}DFT}$ is stationary for Ψ satisfying Eq. (8) and the yielded density satisfies the Eq. (5), the coordinate representation of $\hat{V}_{RC}$ [44] is related to the RC functional via the equation

$$E^p_{RC}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})V^p_{RC}[\rho(\mathbf{r})].$$

However, since Ψ is not a stationary state of $E_{MR\text{-}DFT}$ in general, we have

$$V_{RC}[\rho(\mathbf{r})] = \delta E^p_{RC}[\rho]/\delta\rho(\mathbf{r}). \quad (9)$$

This is just a usual relation employed in MR-DFT [23–25, 27–38, 45, 47]. In our experience, the ground-state energies calculated using these two definitions of $V_{RC}[\rho(\mathbf{r})]$ are similar to each other for first-and-second row atoms, but the difference becomes rather large for molecules where the RC field affects on the CI coefficients of bonding and antibonding configurations. In addition, the deviations become larger when the orbital relaxation effects are taken into account by employing MCSCF-DFT. The situation that the effective solution is not a stationary point of the effective energy is known also in the case of KS-DFT [2].

Unlike the Coulomb-driven MR-DFT developed by Savin and coworkers [27, 29–37], the wavefunction-driven MR-DFT reduces to Hartree–Fock plus DFT correlation correction, not to KS-DFT. This reflects the fact that the full Coulomb operator $\hat{V}_{ee}$ is covered in the modified universal functional, $F^p[\rho(\mathbf{r})]$. This point becomes important when we consider links among several computational schemes.

Extensions to MR-DFT for Excited States

So far, we have been concerned with the ground-state formulation of MR-DFT. The effective CI-DFT equation yields not only ground-state CI solution, but also excited-state solutions. We shall therefore describe the theoretical basis for interpretation of these solutions in this section.

The variational extension of the Hohenberg–Kohn–Levy DFT for excited states is possible using the Levy–Perdew–Lieb (LPL) bifunctional [67, 68] or Theophilou's subspace DFT [69–71]. Both theories have already been applied for KS-DFT by Levy and Nagy [72, 73], and by Nagy [74], respectively.

The LPL theory is based on the bifunctional for the kth excited state

$$F[\rho_0, \rho_k] = \text{Min}^{\perp\{\Psi_i\}_{i=0,\ldots k-1}}_{\Psi\to\rho_k}\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle, \quad (10)$$

where the variational space of the right side is assumed to be orthogonal to the low-lying $k-1$ eigenstates and the constrained search is implemented so that the ground-state density is given by ρ_0 and the kth state density by ρ_k. Defining a modified universal bifunctional as

$$F^p[\rho_0, \rho_k] = \text{Min}^{p\perp\{\Psi_i\}_{i=0,\ldots k-1}}_{\Psi\to\rho_k}\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle, \quad (11)$$

we can derive the effective CI equation for the kth state as

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{ext} + \hat{V}_{RC}[\rho_0, \rho_k])|\Psi\rangle = E^k_{MR\text{-}DFT}|\Psi\rangle, \quad (12)$$

where an index "p" in Eq. (11) has a similar meaning to that in Eq. (5). That is, Ψ is a specific type of CI wave function. Note that the lower-lying states must be projected out from the variational space of Eq. (12).

Another route to MR-DFT for excited states is the use of the subspace DFT developed by Theophilou et al. [69–71]. In the subspace DFT, a variational principle, which is similar to the Hohenberg–Kohn–Levy theorem for one state, holds for the energy functional

$$E_{av:M} = \frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{H}|\Psi_i\rangle = \text{Min}_{\rho_{av:M}(\mathbf{r})}E_{av:M}[\rho_{av:M}(\mathbf{r})] \quad (13)$$

of the average density up to Mth low-lying states

$$\rho_{\text{av:M}}(\mathbf{r}) = \frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{\rho}(\mathbf{r})|\Psi_i\rangle. \qquad (14)$$

Rewriting the minimum average energy to

$$E_{\text{av:M}}^{\text{MR-DFT}} = \text{Min}_{\rho_{\text{av:M}}(\mathbf{r})}\left\{\text{Min}_{\{\Psi_i\}\rightarrow\rho_{\text{av:M}}(\mathbf{r})}^{p}\frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{T}\right.$$

$$\left. + \hat{V}_{ee}|\Psi_i\rangle + \int d\mathbf{r}\rho_{\text{av:M}}(\mathbf{r})V_{\text{ext}}(\mathbf{r}) + E_{\text{RC}}^{p}[\rho_{\text{av:M}}(\mathbf{r})]\right\}, \quad (15)$$

and using the Lagrange multipliers for the constraint that all CI states $\{\Psi_i\}_{i=1}^M$ are orthonormal, we finally obtain the effective CI equation of the subspace MR-DFT as

$$\{\hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}} + \hat{V}_{\text{RC}}^{\text{av:M}}\}|\Psi_i\rangle = E_i|\Psi_i\rangle, \qquad (16)$$

where the coordinate representation of $\hat{V}_{\text{RC}}^{\text{av:M}}$ is defined as the variation of $E_{\text{RC}}^{p}[\rho_{\text{av:M}}]$ with respect to $\rho_{\text{av:M}}(\mathbf{r})$ as usual. In the subspace MR-DFT, the physical quantities are only the average density and its functional. If we intend to estimate the kth excited state energy, we must solve Eq. (16) using average density up to the kth state, and then solve Eq. (16) once more, but with average density up to $(k-1)$th state. Since the results provide the sum of energies up to kth state, $k \times E_{\text{av};k}^{\text{MR-DFT}}$ and to $(k-1)$th state, $(k+1) \times E_{\text{av};k+1}^{\text{MR-DFT}}$ respectively, then the difference is just the kth state energy.

These somewhat complicated procedures to obtain the excited state energies could be skipped if the individual energies obtained from Eq. (16) could approximate the real excited-state energies well. Indeed, we show for several first-and-second row atoms that such "average approximation" of the subspace MR-DFT provides similar excited energies obtained by the LPL functional and original subspace MR-DFT, where the same CI expansion and RC functional are employed [47].

If almost all the state-dependent correlation effects can be covered by a modest CAS wave function, the remaining correlation effects become state-free, being possible to be described by a simple semilocal approximation. Such is a fundamental guideline to construct our previous MR-DFT [45, 47]. When we employ a CAS type of wave function, we followed the prescription proposed by Miehlich, Stoll, and Savin (MSS) [28], and Gräfenstein and Cremer (GC) [41, 42] to prepare an RC functional.

Following a Coulomb division scheme [27], we have proposed another type of MR-DFT where classical Coulomb, exchange, and the long-range part of correlation terms are covered by wave function, the short-range part of correlation by density functional [45]. For this purpose, we introduce the effective two-electron operator to reproduce the classical Coulomb, exchange, and LR part of correlation terms in the context of the CI theory, and use the Savin–Flad–Padè (SFP) prefactor functional to extract the short-range Coulomb driven correlation term. This scheme can be applied for any flexible wave function such as single-double CI and MRCI, without overcounting of electron correlations. Note that all the exchange effects are described by the wave function part in this MR-DFT. The motive to preserve the nonlocal feature of exchange term in both MSS-GC and SFP schemes is that the exchange term is obviously state-and-system dependent, and so must be included in a modified universal functional if we follow the above guideline. In addition, these SIC types (wave function-driven or SFP type) of MR-DFT are also essential to avoid another double counting problem of correlations between semilocal exchange term and RC term [42].

Indeed, the MR-DFT based on this picture works well for correlation of the ground state of atoms and simple molecules. However, the excited energies calculated by using CASCI plus a semilocal DFT residual correction are overestimated for most atoms we examined. For instance, the excited energies of Li and C atoms calculated by the above-mentioned MR-DFT treatments, i.e., LPL, subspace MR-DFT, and its average treatments, for excited states are plotted in Figure 2. For these computations, CASCI-DFT/6-311++G(2df,pd) with modest CASCI and MSS-GC scheme results are presented, but even if we use the SF–Padè scheme, this situation is not improved [47]. The details and applications in this type of "a modest CASCI plus semilocal RC correction method" for other atoms are discussed in Ref. [47]. The feature of these our previous version of MR-DFT is that RC corrections depends only the semilocal character of the density of the states: the RC corrections become larger as the density becomes more contracted. This observation suggests that the matter might not be quite as simple as we expected; i.e., it is not always appropriate to assume that almost all dynamical correlation effects are of state-free. This implies that the some state-dependent RC functional is required for excited states.
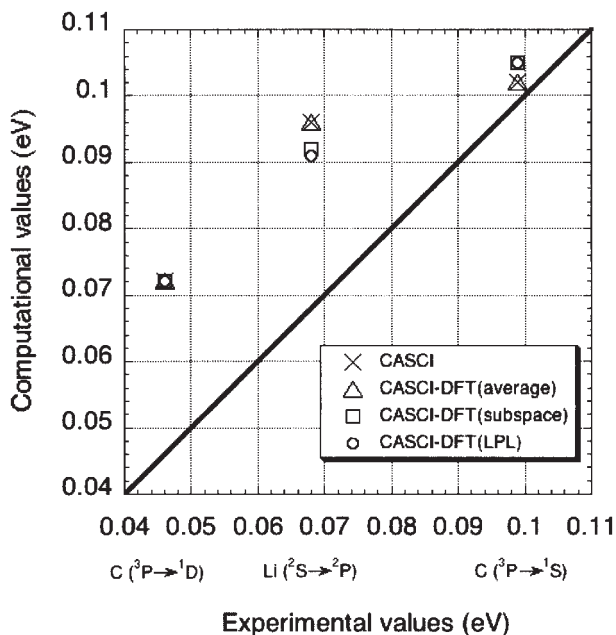
FIGURE 2. Excitation energies of lithium (Li) and carbon (C) atoms calculated by CAS-DFT using semi-local correlation correction. Active spaces are [5, 3], [4, 4] ([orbitals, electrons]) for Li and C, respectively.

To improve a state-free and semi-local E_{RC}^p, one possible way is that another fundamental variable is used for E_{RC}^p. In MR-DFT, after the work by Moscardó and San-Fabián [10], many of developers have employed the on-top pair density, $\rho_2(\mathbf{r}, \mathbf{r})$, which is the probability that two electrons exist at the same point, as a second variant of E_{RC}^p. Indeed, using the on-top pair density or its equivalent one-electron density, we can detect fundamental features of the electronic state, for instance, ionic, radical, and neutral characters as shown previously [43]. Recently, Gusarov et al. [25] suggest the use of $\rho_2(\mathbf{r}, \mathbf{r})$-dependent E_{RC}^p to express the wave function dependency of E_{RC}^p within the framework of the wave function-driven MR-DFT [25]. Their direction is quite promising in MR-DFT.

So far we have been concerned with a MR-DFT using semi-local type of RC corrections as shown in Figure 1(c). The developers of this type of MR-DFT intend to improve in a direction of an arrow illustrated in Figure 1(c). However, it is possible to change a starting point of MR-DFT to the shaded regions in Figure 1(d). Such treatment is appropriate for the case that both of electron correlation types (ii) and (iii) are essential. Thus, in the next section, we propose an orbital-dependent correlation correction for MR-DFT.

Orbital-Dependent Correlation Correction for MR-DFT

At first, we have to determine the many-body perturbation theory as in the context of KS-OEP approach. We shall confine our attention to the MR-based second-order perturbation (PT2) theories [75–84], which is now widely accepted as one of most reliable ab initio methods not only for the ground state, but also for low-lying excited states. The reason for the success of MR-PT2 is that it covers electron correlations of type (ii) and (iii), as illustrated in Figure 1(d), which are remarkably important for molecular systems as described above. The MR-PT methods fall into two types: the diagonalize-then-perturb type [75–79, 81], in which the specific multireference state is corrected using PT, and the perturb-then-diagonalize type [80], in which constructing the effective Hamiltonian using PT for each of its matrix elements, then it is diagonalized to obtain several low-lying states simultaneously. This branch is rather based on quasi-degenerate PT [85, 86] and is desirable for description of the nearly degenerate states such as avoid crossing. However, since the energy expression of MR-DFT is originally of a specific state, or of an average over several states, it is reasonable to choose the former MR-PT.

We recall that a key point of the KS-OEP method is that the orbital-dependent XC potential is obtained via the chain rule for functional derivatives. In the theoretical procedure, the virtual orbitals obtained by the KS equation are also exploited. Thus, the generalization of KS-OEP to a MR version of OEP is not so straightforward: we cannot derive the system of equations by imposing $\delta E[\rho(\mathbf{r})]/\delta V_{RC}(\mathbf{r}) = 0$ with the ICI-DFT equation, at least, in a straightforward way. Instead of this "optimized effective potential method" starting from this equation, "a simple orbital-dependent correlation correction" in MR-DFT is proposed in the following. For simplicity, we limit the discussion to CASSCF-DFT, hereafter. In addition, we also omit the cases that the ground-state and the low-lying states are (quasi-)degenerate to avoid the issues such as the validity of the state-specific CAS-PT2 solutions and/or the intruder-state problem.

The CASCI-DFT equation provides not only the ground-state solution, but excited states as well. These define two spaces, denoted by V_0 and V_{CAS}, the sum space of which is just the limited Hilbert space specified in Eq. (5). However the outer space

that complements to $V_0 + V_{CAS}$ is needed in the context of MR-DFT that mimics CAS-PT2, implying that another auxiliary equation is needed in order to construct the orbital-dependent RC functional. One candidate for this auxiliary equation is the generalized Fock equation, which is a standard starting point for CAS-PT2. The matrix element of the effective Fock operator is given by

$$f_{pq} \equiv \langle p|\hat{h}^{\text{MR-DFT}}|q\rangle + \sum_{rs}\left[\langle pr|qs\rangle - \frac{1}{2}\langle pr|sq\rangle\right]\mathbf{P}_{rs}. \quad (17)$$

The difference from that of the original CAS-PT2 is that the one-electron operator is replaced by $\hat{h}^{\text{MR-DFT}}$, which contains kinetic, external potential, and RC potential operators. As we use a CASSCF-DFT wave function as a reference, the matrix is divided into 3×3 blocks corresponding to inactive, active, and second orbital spaces. This generalized Fock operator of CASSCF-DFT wave function in the matrix form has suitable properties for orbital-dependent correction approach. First, according to the generalized Brillouin theorem, f_{pq} becomes zero when one of the indices represents an inactive and the other a secondly orbital. Second, the unique set of canonical orbitals can be obtained by block-diagonalizing this matrix within three subspaces:

$$\left[-\frac{\Delta_{\mathbf{r}}}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{HF}}(\mathbf{r}) + V_{\text{RC}}(\mathbf{r})\right]\phi_p(\mathbf{r}) = \varepsilon_p\phi_p(\mathbf{r})$$

$$(18a)$$

$$V_{\text{HF}}(\mathbf{r})\phi_p(\mathbf{r}) = \sum_{r,s}\int\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}$$

$$\mathbf{P}_{rs}\left[\phi_r(\mathbf{r}')\phi_s(\mathbf{r}') - \frac{1}{2}\phi_r(\mathbf{r}')P_{\mathbf{r}\mathbf{r}'}\phi_s(\mathbf{r}')\right]\phi_p(\mathbf{r}), \quad (18b)$$

where $\mathbf{P}$ is the first-order spinless reduced density matrix of the CAS-DFT wave function. The important points involved are that all orbitals are orthogonal each other and that the CASSCF-DFT wave function is invariant to this diagonalization.

As the density and the active space, which is the index of $F^p[\rho(\mathbf{r})]$, determine $V_{\text{RC}}(\mathbf{r})$ and $\mathbf{P}$ by virtue of the Hohenberg–Kohn–Levy theorem, the set of orbitals and those orbital energies $\{\phi_p(\mathbf{r}), \varepsilon_p\}$ are also uniquely determined. Further, note that the solutions of equation (18) and those of the effective CASCI equation are expected to converge simulta-

neously when $\mathbf{P}$ converges. Thus, we employ Eq. (18) as a second auxiliary equation in our method.

One can then rewrite the Fock operator in the form

$$\hat{F} = \hat{F}_D + \hat{F}_N = \sum_p \varepsilon_p\hat{E}_{pp} + \sum_{it}(f_{it}\hat{E}_{it} + f_{ti}\hat{E}_{ti})$$

$$+ \sum_{at}(f_{at}\hat{E}_{at} + f_{ta}\hat{E}_{ta}), \quad (19)$$

where $\hat{E}_{pq} \equiv \sum_\sigma a_{p\sigma}^+a_{q\sigma}$ is a spin-averaged excitation operator. The diagonal block parts of Fock operator:

$$\hat{F}_D = \sum_p \varepsilon_p\hat{E}_{pp}, \quad (20)$$

consist of the orbital energies and the creation-and-annihilation operators corresponding to the orbitals in Eq. (18a). The remaining nondiagonal terms in $\hat{F}_N$, complicate the following formulation. In the original CAS-PT2 approach, the inclusion of these terms requires an additional iterative procedure, but the results with and without nondiagonal terms are similar to each other, judging from both the numerical results they have reported [78, 79, 81, 83, 84] and our experience. For this reason, we follow the CAS-PT2 method in the form of the diagonal approximation of Fock operator:

$$\hat{F} = \hat{F}_D = \sum_p \varepsilon_p\hat{E}_{pp}. \quad (21)$$

We separate the ab initio Hamiltonian into the zero-order $\hat{H}_0$ and perturbation, $\hat{V}$,

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad (22)$$

The zeroth-order Hamiltonian $\hat{H}_0$ is defined by the Fock operator given in Eq. (21), and projection operators onto the one-dimensional CAS reference space ($\hat{P}_0$), the complementary space within the CAS expansions ($\hat{P}_{CAS}$), and the space spanned by all other excitations ($\hat{P}_{PT}$) as

$$\hat{H}_0 = \hat{P}_0\hat{F}\hat{P}_0 + \hat{P}_{CAS}\hat{F}\hat{P}_{CAS} + \hat{P}_{PT}\hat{F}\hat{P}_{PT}, \quad (23)$$

where indices, (i, j), (t, u, v), and (a, b) represent the inactive, active, and second orbital space, respectively. The zeroth-order energy of the reference CAS state, $|\Psi_0\rangle$ is given by

$$E_0^{(0)} = \langle \Psi_0 | \hat{H}_0 | \Psi_0 \rangle = \sum_p \varepsilon_p \mathbf{P}_{pp}. \qquad (24)$$

The first-order energy is exactly equivalent to the CAS energy:

$$E_0^{(0)} + E_0^{(1)} = \langle \Psi_0 | \hat{H}_0 + \hat{V} | \Psi_0 \rangle$$

$$= \langle \Psi_0 | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Psi_0 \rangle$$

$$= E_{CAS}. \qquad (25)$$

The second-order energy is then given by

$$E_0^{(2)} = \sum_j^{SD} \frac{|\langle \Psi_0 | \hat{H} | \Psi_j \rangle|^2}{E_0^{(0)} - E_j^{(0)}} \qquad (26)$$

where the summation runs over all single-and-double (SD) excited states from the reference and not included in $V_0 + V_{CAS}$. The zeroth-order energy of a determinant is given by

$$E_j^{(o)} = \sum_p^{occ\ in|\Psi_j\rangle} \varepsilon_p. \qquad (27)$$

Note that even if $|\Psi_j\rangle$ is a configuration state function generated from several determinants with the same occupation, the 0th-order energy is given by Eq. (27).

We now have an alternative expression of the MR-DFT energy using the second-order correlation correction,

$$E_0 = \text{Min}_{\rho(\mathbf{r}) \to N} \left[\text{Min}_{\Psi \to \rho(\mathbf{r})}^p \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right.$$

$$\left. + \int d\mathbf{r} \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + E_0^{(2)}(\{\phi_p[\rho(\mathbf{r})]\}, \{\varepsilon_p[\rho(\mathbf{r})]\}) \right]. \qquad (28)$$

In Eq. (28), RC functional is approximated as

$$E_{RC}[\rho(\mathbf{r})] \cong E_0^{(2)}(\{\phi_p[\rho(\mathbf{r})]\}, \{\varepsilon_p[\rho(\mathbf{r})]\}). \qquad (29)$$

To obtain the RC potential, the functional derivatives using the chain rule,

$$\frac{\delta E_{RC}}{\delta \rho(\mathbf{r})} = \sum_p \int d\mathbf{r}' \left[\int d\mathbf{r}'' \left\{ \frac{\delta E_{RC}}{\delta \phi_p(\mathbf{r}'')} \frac{\delta \phi_p(\mathbf{r}'')}{\delta V_{RC}(\mathbf{r}')} + c.c. \right\} \right.$$

$$\left. + \frac{\delta E_{RC}}{\delta \varepsilon_p} \frac{\delta \varepsilon_p}{\delta V_{RC}(\mathbf{r}')} \right] \frac{\delta V_{RC}(\mathbf{r}')}{\delta \rho(\mathbf{r})}, \qquad (30)$$

must be calculated. First-order perturbation treatment of Eq. (18) gives

$$\frac{\delta \phi_p(\mathbf{r})}{\delta V_{RC}(\mathbf{r}')} = -G_p(\mathbf{r}, \mathbf{r}') \phi_p(\mathbf{r}'), \qquad (31)$$

$$\frac{\delta \varepsilon_p}{\delta V_{RC}(\mathbf{r})} = \phi_p^*(\mathbf{r}) \phi_p(\mathbf{r}) \qquad (32)$$

$$\frac{\delta \rho(\mathbf{r})}{\delta V_{RC}(\mathbf{r}')} = -2 \sum_p^{inactive} \phi_p^*(\mathbf{r}) G_p(\mathbf{r}, \mathbf{r}') \phi_p(\mathbf{r})$$

$$- \sum_p^{active} \sum_r^{active} n_r \psi_r^*(\mathbf{r}) U_{rp} G_p(\mathbf{r}, \mathbf{r}') \phi_p(\mathbf{r}) + c.c. = \chi_{RC}(\mathbf{r}, \mathbf{r}'). \qquad (33)$$

Here, Eq. (33) is the linear response function, $\chi_{RC}(\mathbf{r}, \mathbf{r}')$, of MR-DFT density to residual correlation potential. In Eqs. (31)–(33), $G_p(\mathbf{r}, \mathbf{r}')$ is a Green's function, defined as

$$G_p(\mathbf{r}, \mathbf{r}') \equiv \sum_{q \neq p} \frac{\phi_q^*(\mathbf{r}') \phi_q(\mathbf{r})}{\varepsilon_q - \varepsilon_p}. \qquad (34)$$

$\psi_r(\mathbf{r})$ is a natural orbital of the CAS wave function with the occupation number, n_r ($0 \leq n_r \leq 2$). Note that it belongs to the active space and can be transformed into the solutions within the active space via a unitary transformation:

$$\psi_p(\mathbf{r}) = \sum_r^{active} U_{pr} \phi_r(\mathbf{r}). \qquad (35)$$

Substituting Eqs. (31)–(33) into Eq. (30), we obtain the RC potential that has a form similar to XC potential of KS-OEP,
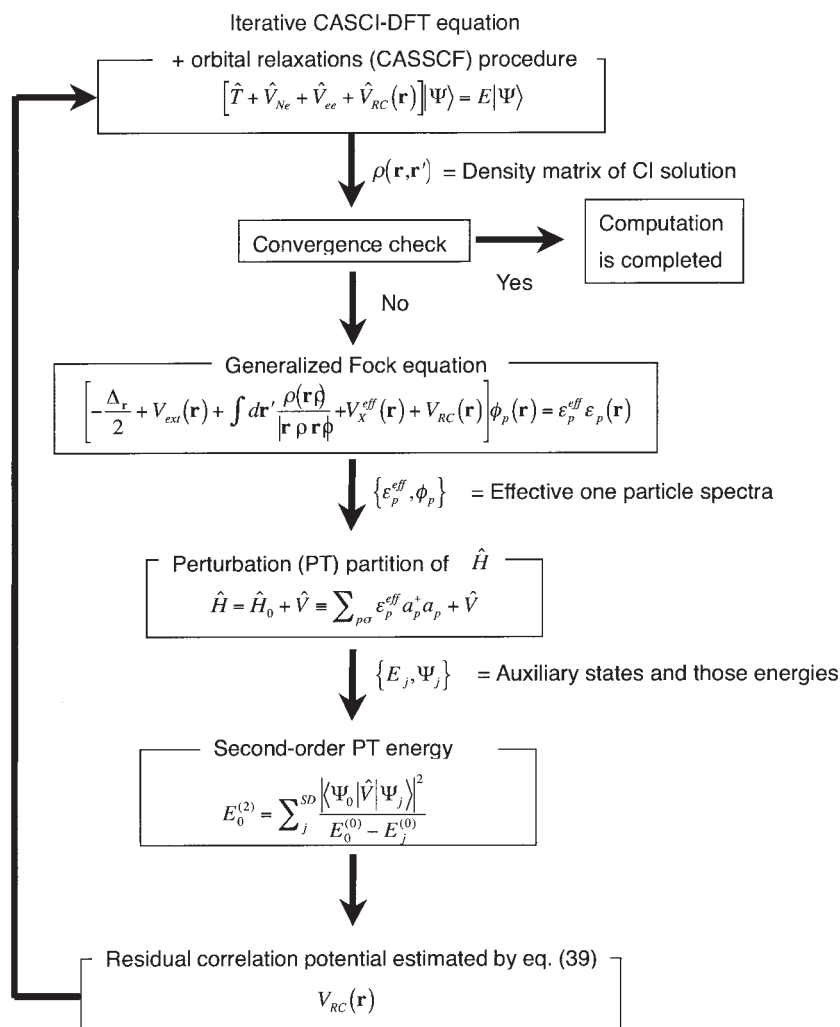
FIGURE 3. Computational scheme of MR-DFT based on CAS-PT2(D) type of approximation.

$$V_{RC}(\mathbf{r}) = \sum_p \int d\mathbf{r}' \left[\int d\mathbf{r}'' \left\{ \frac{\delta E_{RC}}{\delta \phi_p(\mathbf{r}'')} [-G_p(\mathbf{r}'', \mathbf{r}')\phi_p(\mathbf{r}')] \right. \right.$$

$$\left. \left. + c.c. \right\} + \frac{\delta E_{RC}}{\delta \varepsilon_p} |\phi_p(\mathbf{r}')|^2 \right] \chi_{RC}^{-1}(\mathbf{r}, \mathbf{r}'). \quad (36)$$

Here, the constraint that the effective CI wave function is the ground-state solution for $V_{RC}(\mathbf{r})$ is imposed. It should again be noteworthy that the solutions of the effective Fock equation (18) are expected to converge when the effective CI equation is converged after the SCF process. The computational scheme is summarized in Figure 3.

The method presented is free from the so-called double-counting problem involving CAS-

DFT. The connection to usual CAS-DFT scheme is straightforward: if we replace the correlation functional by the explicit semilocal residual correlation like Lee–Yang–Parr correlation multiplied by the MSS-GC prefactor functional, the usual CAS-DFT is obtained. The relationship between the present formalism and the KS-OEP is slightly complicated. When the reference wave function reduces to a single determinant, the effective MR-DFT equation simplifies to the corresponding generalized Fock equation, very similar to KS-OEP equation. Indeed, the above procedure to derive the RC potential becomes similar to an OEP procedure, except that the exchange part is treated in the generalized Fock equation [Eq. (21)].

This single-determinant limit is a result of the previously mentioned fact that the wave function-driven MR-DFT reduces to HF-DFT. This is reasonable from the viewpoint that CAS-PT2 becomes equivalent to Møller–Plesset PT2 when the reference wave function reduces to a single-determinant.

Discussion

We proposed a simple orbital-dependent correlation correction method for MR-DFT based on the CAS-PT2 method. The perturbation term is constructed by exploiting the eigenvalues and eigenfunctions of generalized Fock equation. We note that the formalism presented becomes equivalent to Hartree–Fock theory with correlation correction via optimized effective manner when the reference wave function reduces to a single-determinant. This is because the generalized Fock operator includes the Hartree–Fock exchange operator (not "the exact exchange operator" in OEP). In the OEP theory, multiconfiguration (MC) extensions to treat the multiplet problem have been worked out [87–90]. The working equation of MC-OEP is an effective one-electron equation, but OEP potential is constructed to satisfy a symmetry condition and to include the type (ii) of electron correlation within the KS-OEP framework. To describe the electronic structure involved the correlations that strongly depend on states at both dynamical and nondynamical levels, the types (ii) and (iii) as shown in Figure 1(d) or further all types of correlations in Figure 1(e) may have to be covered. For the purpose, it is a most straightforward way to combine the low-lying CI, DFT and orbital-dependent corrections, i.e., the MR-PT-DFT approach. For instance, a CASPT2-DFT approach can be implemented in the Coulomb-driven type [27, 29–39] or SFP type [45] of MR-DFT. The problem is the computational cost for both MR-DFT with orbital-dependent corrections/MR-PT-DFT. Indeed, although the results of MR-DFT and OEP approaches encourage the applications of MR-DFT with orbital-dependent corrections for molecules, the method presented in the present work is also anticipated to be a cost-consuming approach. However, the efficient techniques developed in both the CAS-PT2 and KS-OEP methods [91, 92] can be used in MR-DFT based on CASPT2. Further, the recently developed divide-and-conquer (DC) framework [93–97] has greatly reduced the computational costs when we apply the ab initio approach for large molecules. If the essential electron correlations are of types (ii) and (iii), and if these correlation lengths are at most the size of a some molecular unit in the large molecule, such a DC method based on electronic structure theory designed for types (ii) and (iii) of electron correlations will become a promising direction in computational chemistry.

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