Highlight Review

Recent Development of Multireference Density Functional Theory

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Abstract

We review a recently developed ab initio multireference (MR)-density functional theory (DFT) approach based on the partially interacting reference systems. Instead of Kohn–Sham equations, we introduce the auxiliary CI equation with the effective DFT potential field. For practice, we classify electrons of the target system into valence electrons and other electrons. The former plays the quantum resonating feature of electronic structure of molecular species, while the latter affects the electronic properties via the effective correlation potential for the former electrons. The theoretical devices in our MR-DFT are introduced to avoid the double counting problem for any combination of a wavefunction and a correlation functional. Some numerical examples are presented.

◆ 1. Introduction

It is well known that the "molecular orbital (MO)" is a fundamental ingredient of chemistry, which enables us not only to understand but also to predict the mechanism of many chemical phenomena.[1] However, the several chemical-and-physical features, such as atomic multiplets,[2] biradical species,[3,4] molecular species exhibiting ion-radical characters,[5,6] etc., are beyond the scope of the simple MO picture. The "resonation"[7] of the several electronic configurations, which is emphasized by Pauling, is another key concept for understanding the functionality and reactivity of chemical compounds in such cases. In the context of ab initio computational chemistry, these two ingredients can be exploited by using the Kohn–Sham (KS) density functional theory (DFT)[8] and by the multireference (MR) wavefunction theory (WFT)[9] such as configuration interaction (CI) theory, respectively. Then, the electron correlation effects are divided into nondynamical and dynamical correlation effects.[10,11] The former corresponds to the concept of "resonation," which obviously reflects the structure of the system. On the other hands, the latter is mainly due to structure-independent correlation effects, which are expected to be covered by an effective field for the MOs. Indeed, in the KS-DFT, electrons occupied up to highest occupied MOs (HOMOs), under the effective exchange-correlation (XC) potential designed so that the XC effects are covered within the single-determinant picture. Despite its great success, the KS-DFT does not work well for the case that the density is not noninteracting v-representable,[12] i.e., the density can not be described by simple MO picture with a single-determinant.[11] Such cases are just situations beyond MO picture cited above. The problem stems from the "resonation" of several configurations of the electronic structure, so a straightforward remedy is to merge a MR-WFT into the DFT, being MR-DFT.

Because the prescription to cover the electron correlation by KS-DFT is quite different to that of the MR-WFT, this is a very difficult issue. The first generation of MR-DFT suffers the severe double counting problem,[13] but recent developers resolve this problem by several ways.[14,15] We contribute to the issue of how to define the spin-polarizability of a singlet MR solution by introducing the radical density and/or ionic density expressed by natural orbitals and those occupations of MR wavefunctions.[16]

Recent developments of MR-DFT's are obviously towards the multireference version of density functional theory.[11,15,17–19] Kusakabe introduces MR-WF in order to define a universal functional of a partially interacting system, deriving the set of equations called "the extended KS-DFT (EKS-DFT)."[19] Savin and his co-workers have developed a MR-DFT based on adiabatic connection by dividing the Coulomb interaction into the short-range and long-range parts.[15] We also present a multireference version of DFT, but the universal functional, of which the definition is a key point of MR-DFT, is defined by exploiting, not the limitation of two-electron term but the extent of wavefunction expansion.[17] The mathematical framework of our MR-DFT is given by a CI equation with a residual density functional correlation potential. It is obvious that the effective CI problem of the MR-DFT should be solved by an iterative manner, so we call it "iterative CI-DFT (ICI-DFT) approach."[17] The setting of ICI-DFT implies that there are two types of electrons: The members of the first type constitute an explicit many-electron system, i.e., cover a resonating picture of the electronic structure. In other words, it is desirable to set valence electrons as these electrons. Other electrons play a backstage role for the valence electrons

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via a residual density functional correlation potential. An important class of MR-DFT is complete-active-space (CAS)-DFT where the CAS wavefunction is employed to treat resonating features completely.[11,14,16,18,19]

We omit the orbital relaxation effect of CAS self-consistent-field (SCF), i.e., use CASCI for wavefunction part of MR-DFT. As for a residual DFT correlation term, we employed two schemes. First one is that developed by Miehlich, Stoll, and Savin (MSS) and Gräfenstein and Cremer (GC),[14] in which we assume CAS type for wavefunction in MR-DFT. Second one is based on the Coulomb partition scheme using Yukawa potential for short-range part,[20] which is suitable for more flexible types of wavefunctions. The explicit residual correlation (RC) functional is the Padè type rational functions yielded by quantum Monte Calro results by Savin and Flad (SF).[20] Further, we introduce an effective two-electron operator into ICI-DFT equation to incorporate the Coulomb partition scheme into our MR-DFT. The computational results of ICASCI-DFT using MSS-GC and SF-Padè schemes on atoms are presented as an illustrative example.

2. Theory

2.1 MR-DFT for Ground State

We first review the fundamental aspect of DFT. The starting point of DFT is the energy expression for ground state,[21]

$$E = Min_{\rho(\boldsymbol{r})\to N}\left[F[\rho(\boldsymbol{r})] + \int \mathrm{d}\boldsymbol{r}\rho(\boldsymbol{r})V_{\mathrm{ext}}(\boldsymbol{r})\right] \tag{1}$$

where $V_{\mathrm{ext}}(\boldsymbol{r})$ is an external potential and $F[\rho(\boldsymbol{r})]$ is the universal functional of Hohenberg–Kohn–Levy,[21] defined as

$$F[\rho(\boldsymbol{r})] = Min_{\Psi\to\rho(\boldsymbol{r})}\langle\Psi|\hat{T} + \hat{V}_{\mathrm{ee}}|\Psi\rangle \tag{2}$$

The corresponding Euler equation is,

$$\frac{\delta F[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = -V_{\mathrm{ext}}(\boldsymbol{r}) + \mu \tag{3}$$

The explicit form of this universal functional is not given, so eq 3 is not a practical equation for computations.

Kohn and Sham[8] enable us to use DFT as a powerful theoretical tool. The setting of KS-DFT is a virtual system where the electrons behave like noninteracting electrons, but under the effective exchange-correlation (XC) potential. Then the universal functional of KS-DFT is the noninteracting kinetic functional as

$$T_{\mathrm{s}}[\rho(\boldsymbol{r})] = Min_{\Phi\to\rho(\boldsymbol{r})}\langle\Phi|\hat{T}|\Phi\rangle \tag{4}$$

$$\begin{aligned} E = Min_{\rho(\boldsymbol{r})\to N}\Bigg[& T_{\mathrm{s}}[\rho(\boldsymbol{r})] + U_{\mathrm{clmb}}[\rho(\boldsymbol{r})] \\ & + E_{\mathrm{XC}}[\rho(\boldsymbol{r})] + \int \mathrm{d}\boldsymbol{r}\rho(\boldsymbol{r})V_{\mathrm{ext}}(\boldsymbol{r})\Bigg] \end{aligned} \tag{5}$$

U_{clmb} and E_{XC} are the classical coulomb, XC terms, respectively. The Euler equation is then given by

$$\frac{\delta T_{\mathrm{s}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = -V_{\mathrm{eff}}^{\text{KS-DFT}}(\boldsymbol{r}) + \mu \tag{6}$$

with the Kohn–Sham effective field defined by

$$V_{\mathrm{eff}}^{\text{KS-DFT}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{\mathrm{XC}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} \tag{7}$$

Now, we shall proceed to MR-DFT. Some of recent developers of MR-DFT first incorporate the part of Coulomb interaction term into the universal functional. For instance, Savin and his co-workers divided the Coulomb operator into short-and-long range parts,

$$\hat{V}_{\mathrm{ee}} = \hat{V}_{\mathrm{ee}}^{\lambda:\mathrm{Long}} + \hat{V}_{\mathrm{ee}}^{\lambda:\mathrm{Short}} \tag{8}$$

leading to an universal functional for a long-range interacting system

$$F^{\lambda}[\rho(\boldsymbol{r})] = Min_{\Psi\to\rho(\boldsymbol{r})}\langle\Psi|\hat{T} + \hat{V}_{\mathrm{ee}}^{\lambda:\mathrm{Long}}|\Psi\rangle \tag{9}$$

They have proposed several options such as the Yukawa potential,[20] the error and erfgau function[15] for eq 8. On the other hand, Kusakabe suggests another reference system, in which the universal functional covers on-site repulsion terms.[19] A reference system is determined by choosing a part of electron repulsion operator covered by a universal functional like eq 9.

In contrast to these "Coulomb-driven" MR-DFTs, we used a "wavefunction-driven" MR-DFT. In other words, the reference system of MR-DFT is defined by choosing a variational space of MR wavefuctions, i.e., a part of N-electrons' Hilbert space,

$$F^{\mathrm{p}}[\rho(\boldsymbol{r})] = Min_{\Psi\to\rho(\boldsymbol{r})}^{\mathrm{p}}\langle\Psi|\hat{T} + \hat{V}_{\mathrm{ee}}|\Psi\rangle \tag{10}$$

The superscript, "p" means that the variational space for constrained search is limited to the specific extent of wavefunction expansions such as CASCI, MR-CI, etc. An alternative expression of energy functional becomes

$$\begin{aligned} E_0 = Min_{\rho(\boldsymbol{r})\to N}\Bigg[& F^{\mathrm{p}}[\rho(\boldsymbol{r})] + E_{\mathrm{RC}}[\rho(\boldsymbol{r})] \\ & + \int \mathrm{d}\boldsymbol{r}\rho(\boldsymbol{r})V_{\mathrm{ext}}(\boldsymbol{r})\Bigg] \end{aligned} \tag{11}$$

Obviously, this equation holds from eq 1: We can define the implicit residual correlation (RC) functional, $E_{\mathrm{RC}}[\rho(\boldsymbol{r})]$ as $F[\rho(\boldsymbol{r})] - F^{\mathrm{p}}[\rho(\boldsymbol{r})]$. Although it is not clear whether $E_{\mathrm{RC}}[\rho(\boldsymbol{r})]$ can be described by an explicit density functional, we shall approximate it as semilocal density functional as presented in the later section. An Euler equation using this modified universal functional becomes a similar form to the original (Hohenberg–Kohn–Levy) DFT as

$$\delta F^{\mathrm{p}}[\rho(\boldsymbol{r})]/\delta\rho(\boldsymbol{r}) = -V_{\mathrm{eff}}^{\text{MR-DFT}}(\boldsymbol{r}) + \mu \tag{12}$$

but the RC term is included in the potential

$$V_{\mathrm{eff}}^{\text{MR-DFT}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + \frac{\delta E_{\mathrm{RC}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} \tag{13}$$

We here assume both of the modified universal functional and the RC functional are differentiable. The effective CI-DFT equation is given by

$$(\hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{ext}} + \hat{V}_{\mathrm{RC}})|\Psi\rangle = E_{\text{MR-DFT}}|\Psi\rangle \tag{14}$$

Here, $\hat{T}$ and $\hat{V}_{\mathrm{ext}}$ are the kinetic and the external potential operators, respectively. The coordinate representation of the RC potential, $\hat{V}_{\mathrm{RC}}$ is given by

$$V_{\mathrm{RC}}(\boldsymbol{r}) = \delta E_{\mathrm{RC}}[\rho(\boldsymbol{r})]/\delta\rho(\boldsymbol{r}) \tag{15}$$

In Table 1, we summarize fundamental features of the original

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Table 1. Fundamental features among the original (Hohenberg–Kohn–Levy's) DFT, Kohn–Sham-DFT, and multireference-DFT

	Hohenberg–Kohn–Levy DFT	Kohn–Sham DFT	Multireference DFT
Reference system	Real system	Noninteracting system	Partially interacting system
Universal functional	$F[\rho(\boldsymbol{r})] = Min_{\Psi\to\rho(\boldsymbol{r})}\langle\Psi\vert\hat{T}+\hat{V}_{\mathrm{ee}}\vert\Psi\rangle$	$T_{\mathrm{s}}[\rho(\boldsymbol{r})] = Min_{\Phi\to\rho(\boldsymbol{r})}\langle\Phi\vert\hat{T}\vert\Phi\rangle$	$F^{\mathrm{p}}[\rho(\boldsymbol{r})] = Min^{\mathrm{p}}_{\Psi\to\rho(\boldsymbol{r})}\langle\Psi\vert\hat{T}+\hat{V}_{\mathrm{ee}}\vert\Psi\rangle$
Euler equation	$\dfrac{\delta F[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = -V_{\mathrm{ext}}(\boldsymbol{r})+\mu$	$\dfrac{\delta T_{\mathrm{s}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = -V_{\mathrm{eff}}^{\text{KS-DFT}}(\boldsymbol{r})+\mu$	$\dfrac{\delta F^{\mathrm{p}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = -V_{\mathrm{eff}}^{\text{MR-DFT}}(\boldsymbol{r})+\mu$
Effective field	$V_{\mathrm{eff}}^{\text{HKL-DFT}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r})$	$V_{\mathrm{eff}}^{\text{KS-DFT}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}'\dfrac{\rho(\boldsymbol{r}')}{\vert\boldsymbol{r}-\boldsymbol{r}'\vert} + \dfrac{\delta E_{\mathrm{XC}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})}$	$V_{\mathrm{eff}}^{\text{MR-DFT}}(\boldsymbol{r}) = V_{\mathrm{ext}}(\boldsymbol{r}) + \dfrac{\delta E_{\mathrm{RC}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})}$
Variational ingredient	Density	Kohn–Sham orbital coefficients	CI coefficients (and molecular orbital coefficients[a]).

[a] MCSCF-DFT

(Hohenberg–Kohn–Levy's) DFT, KS-DFT, and MR-DFT.

Since the RC potential $\hat{V}_{\mathrm{RC}}$ depends on the density of CI solutions, Eq 14 must be solved to be self-consistent. We omit the spin-dependency of the RC in Eqs 14 and 15 in order to avoid symmetry broken feature due to a fictitious effective magnetic field like KS-DFT. This is critically different to our previous study.[16]

2.2 *MR-DFT for Excited State*

There are two options if we intend to derive MR-DFT for excited states via a variational manner. First one is based on the Levy–Perdew–Lieb's (LPL) bifunctional[12,22] for kth excited state,

$$F[\rho_0,\rho_k] = Min_{\Psi\to\rho_k}^{\perp\{\Psi_i\}_{i=0,\ldots,k-1}}\langle\Psi|\hat{T}+\hat{V}_{\mathrm{ee}}|\Psi\rangle \tag{16}$$

Here, the variational space of the right side is limited to be orthogonal to up to $k-1$ eigenstates under the constraints that the ground-state density is given by ρ_0 and the kth state density by ρ_k. Then, the minimization of kth state energy is given by

$$E_k = Min_{\rho_k}\left[F[\rho_0,\rho_k] + \int \mathrm{d}\boldsymbol{r}V_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})\right] \tag{17}$$

Levy and Nagy have developed the variational KS-DFT for excite states based on the LPL bifunctional.[23] The MR-DFT implementation of LPL theory is straightforward as follows: We start from the modified universal bifunctional,

$$F^{\mathrm{p}}[\rho_0,\rho_k] = Min_{\Psi\to\rho_k}^{\mathrm{p}\perp\{\Psi_i\}_{i=0,\ldots,k-1}}\langle\Psi|\hat{T}+\hat{V}_{\mathrm{ee}}|\Psi\rangle \tag{18}$$

Here, an additional "p" has a similar meaning to that in Eq 10. That is, Ψ is a specific type of CI wavefunction, which yields the density, ρ_k. Then, the effective CI equation is given by

$$(\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V}_{\mathrm{ext}}+\hat{V}_{\mathrm{RC}}[\rho_0,\rho_k])|\Psi\rangle = E^k_{\text{MR-DFT}}|\Psi\rangle \tag{19}$$

This is similar to eq 14, but note that the lower-lying states must be projected out from the variational space of eq 19.

A second MR-DFT for excited states is based on the subspace DFT developed by Theophilou et al.[24] The generalized ensemble DFT has also been developed.[25] In the Theophilou's theory, a variational principle of the energy functional

$$E_{\mathrm{av}} = \frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{H}|\Psi_i\rangle = Min_{\rho_{\mathrm{av}}(\boldsymbol{r})}E_{\mathrm{av}}[\rho_{\mathrm{av}}(\boldsymbol{r})] \tag{20}$$

for the average density up to Mth low-lying states

$$\rho_{\mathrm{av}}(\boldsymbol{r}) = \frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{\rho}(\boldsymbol{r})|\Psi_i\rangle \tag{21}$$

holds. Here, $\hat{H}$ is a usual ab initio Hamiltonian. Nagy applies this theory for the KS-DFT.[26] The MR-DFT formalism of Theophilou's work is as follows. The average energy functional is defined for the specific CI wavefunctions,

$$E_{\mathrm{av}}^{\text{MR-DFT}} = Min_{\rho_{\mathrm{av}}(\boldsymbol{r})}\left[Min^{\mathrm{P}}_{\{\Psi_i\}\to\rho_{\mathrm{av}}(\boldsymbol{r})}\frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{T}+\hat{V}_{\mathrm{ee}}|\Psi_i\rangle + \int \mathrm{d}\boldsymbol{r}\rho_{\mathrm{av}}(\boldsymbol{r})V_{\mathrm{ext}}(\boldsymbol{r}) + E_{\mathrm{RC}}[\rho_{\mathrm{av}}(\boldsymbol{r})]\right] \tag{22}$$

Here, $\{\Psi_i\}_{i=1}^{M}$ are the M low-lying CI solutions, of which the average density is given by $\rho_{\mathrm{av}}(\boldsymbol{r})$. Note that the energy of the average of $\{\Psi_i\}_{i=1}^{M}$, not of an individual state, is minimized within the specific variational space of CI,

$$E_0 = Min^{\mathrm{P}}_{\{\Psi_i\}} \times \left[\frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V}_{\mathrm{ext}}(\boldsymbol{r})|\Psi_i\rangle + E_{\mathrm{RC}}[\rho_{\mathrm{av}}(\boldsymbol{r})]\right] \tag{23}$$

under the orthogonal conditions,

$$\langle\Psi_i|\Psi_j\rangle = \delta_{ij} \tag{24}$$

Then, the minimization of Lagrangian,

$$L[\{\Psi_i\}] = \frac{1}{M}\sum_{i=1}^{M}\langle\Psi_i|\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V}_{\mathrm{ext}}(\boldsymbol{r})|\Psi_i\rangle + E_{\mathrm{RC}}[\rho_{\mathrm{P}}(\boldsymbol{r})] - \sum_{ij}^{M}E_{ij}(\delta_{ij}-\langle\Psi_i|\Psi_j\rangle) \tag{25}$$

leads to the equation,

$$\left\{\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V}_{\mathrm{ext}}(\boldsymbol{r})+\frac{\delta E_{\mathrm{RC}}}{\delta\rho_{\mathrm{av}}}(\boldsymbol{r})\right\}|\Psi_i\rangle = \sum_{ij}^{M}E_{ij}|\Psi_j\rangle \tag{26}$$

Since the average observable is invariant for any unitary transformation among $\{\Psi_i\}_{i=1}^{M}$,[24] then the effective CI equation can be rewritten as,

$$\left\{\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V}_{\mathrm{ext}}(\boldsymbol{r})+\frac{\delta E_{\mathrm{RC}}}{\delta\rho_{\mathrm{av}}}(\boldsymbol{r})\right\}|\Psi_i\rangle = E_i|\Psi_i\rangle \tag{27}$$

This MR-DFT formulation of subspace DFT reminds us the Katriel's suggestion that the subspace DFT is similar to the original DFT using the super-Hamiltonian interpretation.[27]

It should be noted that the average density and average energy obtained by solving eq 27 are of real systems, but the individual densities and energies are not. To estimate the kth excited-state energy, we must first solve eq 27 using average density up to kth state, and then solve eq 27 once more, but with average density up to $(k-1)$th state. Since these results provide the sum of energies up to kth state, $\sum_{i=1}^{k} E_i$ and to $(k-1)$th state, $\sum_{i=1}^{k-1} E_i$, respectively, the difference is just the kth state energy, E_k. Instead of this troublesome procedure, it might be possible to approximate the individual energies of eq 27 as the real excited-state energies. This type of approximation is known in the average MCSCF computation.[28]

The remaining problem is how to obtain the residual correlation functional for kth state density in eq 19 and for average density in Eq 27. A possible answer is the use of the RC functional designed for the ground state. This is expected to be valid if we can pack all of the state-specific correlation effects into the universal (bi)functional of MR-DFT so that the remaining correlations are of state-free. Thus, the explicit forms of RC functionals for ground state that will be discussed in the next section, are expected to be transferred to the excited states MR-DFT.

2.3 *Residual Correlation Functionals*

We choose two types of residual correlation functionals developed by precursors. First one is proposed by Miehlich, Stoll, and Savin (MSS), and subsequently Gräfenstein and Cremer (GC).[14] In this method, we introduce a measure of active space and have constructed a prefactor for the correlation term to filter out the electron correlation contributed from CAS wavefunction. The MSS-GC scheme works well for CAS-DFT.[14,16] For instance, we show the previous computational results[16] of energy-corrected version of CASCI-DFT in Figure 1. As shown in this figure, the deviations to experimental bond-lengths for some molecules are improved by CASCI-DFT. However, this MSS-GC scheme can be applied only for CAS wavefunctions.

For MR-DFT with a more flexible wavefunction, we introduce the technique of "Coulomb-driven" MR-DFT, i.e., division of the Coulomb operator. Now, we shall use the Yukawa type of potential[20] for this purpose. In order to exploit this Coulomb division only for double counting prescription, we need a little device.

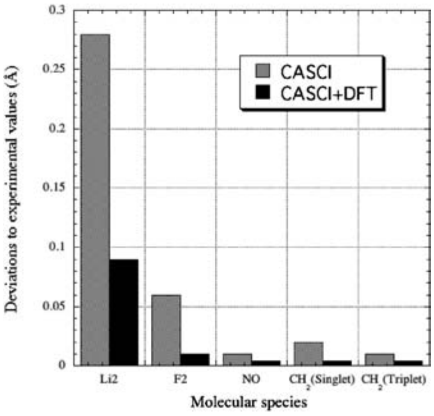

Figure 1. The deviations of bond distances optimized by CASCI and CASCI-DFT methods to experimental ones for some molecules.

First, the exact electron interaction term is approximated as

$$\begin{aligned}\langle\Psi_{\rho}^{\text{exact}}|\hat{V}_{\text{ee}}|\Psi_{\rho}^{\text{exact}}\rangle &\cong U_{\text{clmb}}^{\text{MR}}[\rho(\boldsymbol{r})] + E_{\text{X}}^{\text{MR}}[\rho(\boldsymbol{r})]\\ &+ \frac{1}{2}\int\frac{\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2}{\boldsymbol{r}_{12}}\rho(\boldsymbol{r}_1)[(1-e^{-\alpha r_{12}})\rho_{\text{C}}^{\text{MR}}(\boldsymbol{r}_1,\boldsymbol{r}_2)]\\ &+ E_{\text{RC}}[\rho(\boldsymbol{r})] \end{aligned} \tag{28}$$

Here, the classical Coulomb term, $U_{\text{clmb}}^{\text{MR}}[\rho(\boldsymbol{r})]$, the exchange term, $E_{\text{X}}^{\text{MR}}[\rho(\boldsymbol{r})]$, and long-range part of correlation term (the third term at the right side) are covered by the wavefunction. Obviously, the last term at the right side, which is just a RC functional, is due to the short-range part. Thus, if we design $E_{\text{RC}}[\rho(\boldsymbol{r})]$ so as to cover the short-range Coulomb-driven correlation, the over-counting of electron correlation can be avoided for any MR wavefunction. For this purpose, we follow a simple form of RC functional by Savin and Flad,[20] which is given by the product of usual DFT correlation functional and its prefactor,

$$E_{\text{RC}}[\rho(\boldsymbol{r})] \cong C_{\text{prefactor}}[\rho(\boldsymbol{r})]E_{\text{C}}[\rho(\boldsymbol{r})] \tag{29}$$

They also provide the ratio of short-range part to the whole Coulomb operator on electron correlation using quantum Monte-Carlo computations, but the explicit prefactor functional is not given. Thus, we apply the Padè[3,4] approximation for their numerical data, leading to the prefactor functional,

$$C_{\text{prefactor}}[\rho(\boldsymbol{r})] = \frac{1 + a_1 r_{\text{s}} + a_2 r_s^2 + a_3 r_s^3}{1 + a_4 r_{\text{s}} + a_5 r_s^2 + a_6 r_s^3 + a_7 r_s^4} \tag{30}$$

where $r_{\text{s}} = [3\pi/4\rho]^{1/3}$. An important point is that this type of RC functional can be applied for any combination of a wavefunction and a correlation functional. Hereafter, we call this prescription "Savin–Flad (SF)–Padè approach."

In order to estimate the first three terms at the right side, we now defined the effective two-electron operator

$$\hat{V}_{\text{ee}}^{\text{eff}} \equiv \sum\nolimits_{K}|K\rangle\langle K|\hat{V}_{\text{Clmb}}^{\text{CI}} + \hat{V}_{\text{ex}}^{\text{CI}} + \hat{V}_{\text{c}}^{\text{CI}}|K\rangle\langle K| \tag{31}$$

Here, $\hat{V}_{\text{Clmb}}^{\text{CI}}$, $\hat{V}_{\text{ex}}^{\text{CI}}$, and $\hat{V}_{\text{c}}^{\text{CI}}$ are classical Coulomb, exchange, and correlation operators for CI wavefunction, respectively as

$$\begin{aligned}\hat{V}_{\text{Clmb}}^{\text{CI}} &= \frac{1}{2}\sum\nolimits_{d}^{\text{deg enercy}}\\ &\times \sum\nolimits_{ijkl\sigma\sigma'} a_{j\sigma}^{+}a_{i\sigma}|\Psi_{K,d}^{\text{CI}}\rangle\langle\Psi_{K,d}^{\text{CI}}|a_{l\sigma'}^{+}a_{k\sigma'}\langle ik|jl\rangle \end{aligned} \tag{32}$$

$$\begin{aligned}\hat{V}_{\text{X}}^{\text{CI}} &= -\frac{1}{2}\sum\nolimits_{d}^{\text{deg enercy}}\\ &\times \sum\nolimits_{ijkl\sigma} a_{j\sigma}^{+}a_{i\sigma}|\Psi_{K,d}^{\text{CI}}\rangle\langle\Psi_{K,d}^{\text{CI}}|a_{l\sigma}^{+}a_{k\sigma}\langle ij|kl\rangle \end{aligned} \tag{33}$$

$$\begin{aligned}\hat{V}_{\text{c}}^{\text{CI}} &= \frac{1}{2}\sum\nolimits_{ijkl\sigma\sigma'}\Bigg[a_{j\sigma}^{+}a_{i\sigma}a_{l\sigma'}^{+}a_{k\sigma'} - a_{j\sigma}^{+}a_{i\sigma}\\ &\times \sum\nolimits_{d}^{\text{deg enercy}}|\Psi_{K,d}^{\text{CI}}\rangle\langle\Psi_{K,d}^{\text{CI}}|a_{l\sigma'}^{+}a_{k\sigma'}\\ &+ a_{k\sigma}^{+}a_{i\sigma}\sum\nolimits_{d}^{\text{deg enercy}}|\Psi_{K,d}^{\text{CI}}\rangle\langle\Psi_{K,d}^{\text{CI}}|a_{l\sigma'}^{+}a_{j\sigma'}\delta_{\sigma\sigma'}\Bigg]\langle ik|jl\rangle^{l} \end{aligned} \tag{34}$$

Here, $a_{i\sigma}^{+}$, $a_{j\sigma}$ are the creation and destruction operators for i-th and j-th MOs, respectively. $\langle ik|jl\rangle^{l}$ is a molecular integral

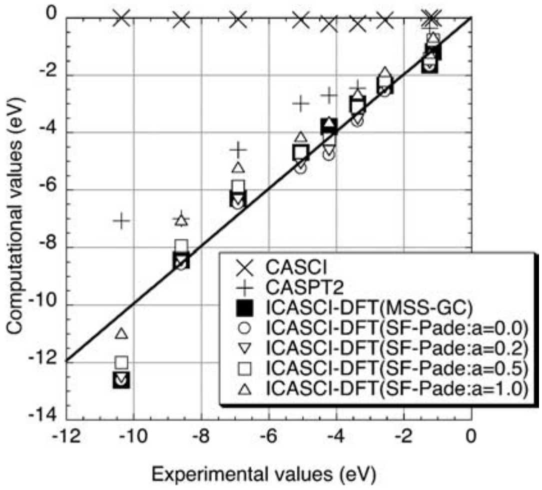

Figure 2. Computational results of ICASCI-DFT, together with CASCI, CASPT2, and experimental results on first-and second-row atoms.

for long-range part of Coulomb repulsion in the physicist's notation,[9]

$$\langle ik|jl\rangle^{l} = \int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \phi_i(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_2)\frac{1-e^{-\alpha r_{12}}}{\boldsymbol{r}_{12}}\phi_j(\boldsymbol{r}_1)\phi_l(\boldsymbol{r}_2) \quad (35)$$

and the $\langle ik|jl\rangle$ is the corresponding original Coulomb repulsion integral. These operators are designed to provide the following expressions of classical Coulomb and exchange terms[9]

$$U_{\mathrm{clmb}}^{\mathrm{MR}:K}[\rho(\boldsymbol{r})] = \frac{1}{2}\int \frac{d\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2}{\boldsymbol{r}_{12}} \rho_{\mathrm{MR}:K}(\boldsymbol{r}_1)\rho_{\mathrm{MR}:K}(\boldsymbol{r}_2) \quad (36)$$

$$E_{\mathrm{X}}^{\mathrm{MR}:K}[\rho(\boldsymbol{r})] = -\frac{1}{2}\sum_{\sigma}\int \frac{\mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2}{\boldsymbol{r}_{12}} \rho_{\mathrm{MR}:K}(\boldsymbol{r}_1,\sigma;\boldsymbol{r}_2\sigma) \times \rho_{\mathrm{MR}:K}(\boldsymbol{r}_2\sigma;\boldsymbol{r}_1\sigma) \quad (37)$$

when we take expectation values in the kth state. Note here that if the target state is N-fold degenerate, the density and density matrix must be averaged over all of those N-fold states. These correspond to the summation over d in eqs 32–34.

Therefore, the explicit form of the effective CI-DFT equation for the SF-Padè scheme becomes

$$\hat{H}_{\mathrm{ICI\text{-}DFT}}|\Psi\rangle = E_{\mathrm{ICI\text{-}DFT}}|\Psi\rangle \quad (38)$$

with the effective Hamiltonian,

$$\hat{H}_{\mathrm{ICI\text{-}DFT}} \equiv \sum_{I,J}|I\rangle\langle I|\hat{T} + \hat{V}_{\mathrm{ee}}^{\mathrm{eff}} + \hat{V}_{\mathrm{ext}} + \hat{V}_{\mathrm{RC}}|J\rangle\langle J| \quad (39)$$

2.4 *Sample Calculations*

The effectiveness of our MR-DFT approaches is checked in the simple numerical examples. For molecular integrals of Yukawa potential, we use Ugalde and Sarasola's code[29] merged into GAMESS.[30] We performed other computations by using our MR-DFT code. Figure 2 shows the correlation energies of first- and second-row atoms: The horizontal axis is the experimental result[31] and the vertical line is the corresponding computational values. The restricted HF (RHF) and restricted open HF (ROHF) canonical orbitals are used for molecular orbitals of MR-DFT calculations with 6-311++G(2df,pd) basis. We choose minimum active spaces for CASCI $[n,m]$ (n electrons, m orbitals) computations. The minimum means that active orbitals are over only smallest valence electrons, but so that CASCI solutions do not reduce to RHF/ROHF solutions, or do not remain arbitrariness due to selections of 2p orbitals. This choice reflects the small correlation corrections of CASCI for all atoms. The correlation energies covered by CASPT2 are considerably larger than the minimum CASCI, but those values are at most 75% (CASPT2 for Be) of experimental ones. On the other hands, the ICASCI-DFT with MSS-GC results show excellent agreements with experimental ones for all atoms. On the other hand, the correlation energies of ICASCI-DFT with SF-Padè scheme strongly depend on screened parameter α of Yukawa potential. This is because we fixed CASCI part of MR-DFT for any α: α^{-1} is a correlation-length of the short-range repulsion, which is covered by DFT part. Therefore, as α increases, the correlation energies of MR-DFT are expected to be decreased. Indeed, the results show such behavior for various. We can see from this figure that the correlation energies are overestimated for the infinite correlation length ($\alpha^{-1} \to \infty$) for most of atoms, and reasonable correlation lengths exists in the range of 1–5 hartree.

◆ 3. Summary

We reviewed the recently developed MR-DFT. In contrast to our previous CAS-DFT, which is only the energy correction to CASCI method using DFT correlation, we developed the iterative CI-DFT approach. The features are that (i) it is a "wavefunction-driven" MR-DFT and that (ii) it can be applied for any combination of a wavefucntion and a DFT correlation functional if the SF-Padè scheme is employed. From a fundamental aspect, it is just one class of DFTs, where the CI coefficients are used to vary the density. As for numerical results, the iterative CASCI-DFT with MSS-GC-LYP RC functional reproduces the qualitative correlation energies for all of atoms. The results of ICASCI-DFT with the SF-Padè scheme are also excellent, but considerably depend on the Yukawa parameter, i.e., the correlation length for RC potential. This is not a disappointing feature from the viewpoint of practical computations. Indeed, the parameter of a screened potential could be fixed to reproduce excellent results like screened Coulomb hybrid functional.[32,33] Finally, we summarized the schematic illustration of recent developed MR-DFTs together with related methods in Figure 3. The Ψ and ρ in 2 × 2 unit indicate that wavefunction and density

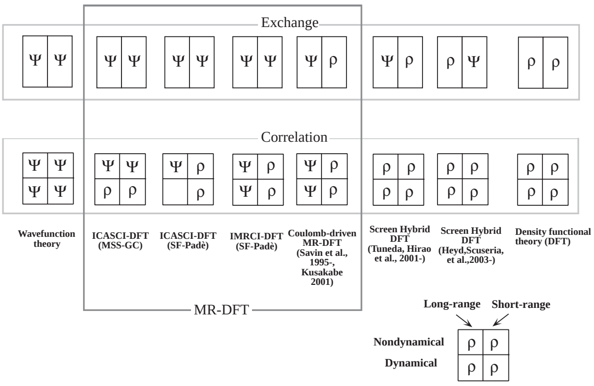

Figure 3. The features of the recent developed MR-DFTs together with, WFT, KS-DFT, and screen Hybrid-DFTs.

functional are used to cover the part of electron correlations, respectively. The vertical partition is for nondynamical/dynamical correlation effects and the horizontal partition for long-range/short-range parts of Coulomb division. In the screened Coulomb hybrid DFT, the long- or short-range part of exchange term is covered by the exact HF term, while all part of correlation is covered by the pure DFT. In contrast, there are two types of MR-DFTs, i.e., "wavefunction-driven" and "Coulomb-driven" MR-DFTs as reviewed in this article. Usual "wavefunction-driven" MR-DFT is irrelevant to the partition of Coulomb division as shown in the MSS-GC unit. On the other hands, it is inevitable to divide both exchange and correlation terms into long-and-short range parts in a pure "Coulomb-driven" MR-DFT. We employ this Coulomb partition only to adopt a more flexible wavefunction in our MR-DFT (IMRCI-DFT with SF-Padè scheme). If we note that α^{-1}, is the correlation length, the correlation factor approach[34] could be used to construct a α-dependent RC functional. Such an approach combined with ICI-DFT is one direction of the practical method of ICI-DFT.

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