Abstract

In 2009, the authors implemented the linear-scaling divide-and-conquer (DC) methods into the GAMESS quantum chemistry package. This program enabled fast energy calculations of closed-shell large molecules with high accuracy in Hartree-Fock (HF), density functional theory, and post-HF levels of theory. After the first implementation, we extended the applicability of the DC scheme into several directions. In this Paper, we summarized recent and future developments in the DC code in GAMESS, namely, the energy gradient methods and open-shell treatments.

Keywords: divide-and-conquer method; self-consistent field calculation; open-shell system; electron correlation; energy gradient

1. Introduction

Since 1980s, many types of accelerating techniques for \textit{ab initio} electronic structure calculations have been developed to treat large molecules [1,2]. In the Hartree–Fock (HF) and density functional theory (DFT) calculations, there are two obstacles to the application to large systems: the construction and the diagonalization of the Fock matrix. A number of methods accelerating Fock construction have been proposed and implemented into many quantum chemistry programs. For accelerating the step of Fock diagonalization, Yang and Lee [3] firstly proposed the divide-and-conquer (DC) method. Recently, the authors have developed the DC code that can treat HF exchange interaction [4,5] and extended the scheme into the post-HF electron correlation calculations [6–9] by applying the energy density analysis (EDA) [10]. The program of the DC method became available in a part of GAMESS package [11,12] from 2009 [13]. The DC-based linear-scaling electronic structure methods are summarized in the review article [14].

After the first implementation, we have extended the DC method to various directions. In this Paper, we present two of these recent developments, namely, the open-shell treatment using unrestricted molecular orbitals (MOs)
[15,16] and a novel energy gradient expression for DC-HF and DC-DFT [17].

2. Extension of DC method

2.1. Open-shell treatment

In the DC method, the system under consideration is spatially divided into disjoint subsystems, called the central region, and the density of the subsystem is constructed from the subsystem MOs. To improve the description of the subsystem density, atoms adjacent to the central region, called the buffer region, are taken into consideration when constructing subsystem MOs. In open-shell calculations using unrestricted MOs, up- and down-spin MOs are determined separately. Subsystem $\sigma$-spin MOs are obtained by solving the following local Pople–Nesbet equations:

$$
P^{\sigma}_{\mu\nu} = \rho^{\sigma}_{\mu\nu} \sum_q \int d\rho \left( \frac{\rho^{\sigma}_{q\mu} - \rho^{\sigma}_{q\nu}}{1 + \exp(-\beta\epsilon)} \right) C^{\sigma \alpha}_{q\mu} C^{\sigma \alpha\ast}_{q\nu}.
$$

Here, $C_q$ and $\epsilon_q$ are the subsystem MO coefficient vector and energy, respectively. $S^{\sigma}$ and $F^{\sigma}$ represent local overlap and $\sigma$-spin Fock matrices for subsystem $\sigma$ that are the submatrices of the entire overlap and Fock matrices. The density matrix of the subsystem $\alpha$, $P^{\alpha}$, is constructed from subsystem MOs as:

$$
P^{\sigma}_{\mu\nu} = \rho^{\sigma}_{\mu\nu} \sum_q \int d\rho \left( \frac{\rho^{\sigma}_{q\mu} - \rho^{\sigma}_{q\nu}}{1 + \exp(-\beta\epsilon)} \right) C^{\sigma \alpha}_{q\mu} C^{\sigma \alpha\ast}_{q\nu}.
$$

with Fermi function $f_{\beta}(\epsilon) = \left[ 1 + \exp(-\beta\epsilon) \right]^{-1}$, $\sigma$-spin Fermi level $\epsilon^{\sigma}_{q\mu}$, and the partition matrix represented by

$$
\rho^{\sigma}_{\mu\nu} = \begin{cases} 
1 & [\mu \in \alpha \land \nu \in \alpha] \\
1/2 & [\mu \in \alpha \land \nu \notin \alpha] \lor [\mu \notin \alpha \land \nu \in \alpha] \\
0 & \text{otherwise}.
\end{cases}
$$

Each $\sigma$-spin Fermi level $\epsilon^{\sigma}_{q\mu}$ is determined by the constraint for keeping the number of $\sigma$-spin electrons. The density matrix of the entire system, $P^{DC}$, is obtained by summing up subsystem contributions as

$$
P^{DC}_{\mu\nu} = \sum_{\alpha} P^{\alpha}_{\mu\nu}.
$$

The self-consistent field (SCF) iterations are carried out until both up- and down-spin density matrices converge. There, Fock matrix and the total energy are calculated by using the density matrices in the standard manner.

We further develop DC-based unrestricted second-order Möller–Plesset perturbation (DC-UMP2) code [17], which is the straightforward extension of the DC-based correlation method for closed-shell systems [6]. In the DC-UMP2 method, the total correlation energy is evaluated by summing up correlation energies of the subsystems:

$$
\Delta E^{\alpha}_{DC-UMP2} = \sum_{\alpha} \Delta E^{\alpha}_{MP2}.
$$

The correlation energy of subsystem $\alpha$, $\Delta E^{\alpha}_{MP2}$, is estimated using subsystem orbitals constructed in the DC-UHF calculation with the assistance of the idea of EDA as follows:

$$
\Delta E^{\alpha}_{MP2} = \sum_{\alpha} \sum_{\sigma} \sum_{i^\alpha,j^\alpha} \sum_{a^\sigma,b^\sigma} \sum_{\mu\nu=S(\alpha)} C^{\sigma \alpha\ast}_{\mu i^\alpha} \left\langle \mu \left| j^\alpha \left| a^\sigma b^\sigma \right. \right. \right\rangle \left( \tilde{\tau}^{\alpha}_{i^\alpha,j^\alpha} \right. \left. \left. \tilde{\tau}^{\alpha}_{i^\alpha,j^\alpha} \right. \left. \right. \right. \left. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \r
where $S(\alpha)$ represents the set of basis functions in the subsystem $\alpha$.

This procedure is applicable to the DFT calculations with the double-hybrid exchange-correlation functional, e.g., B2PLYP [18]. In B2PLYP calculations, the MP2-type correlation energy expression is mixed to the Lee–Yang–Parr (LYP) correlation functional [19], as well as the HF exchange term mixed to the Becke 88 (B88) exchange functional [20]. The energy expression for the B2PLYP functional is then given by:

$$E_{\text{xc}} = (1-a_x)E_{\text{xc}}^{\text{B88}} + a_x E_{\text{xc}}^{\text{MP2}} + (1-a_c)E_{\text{xc}}^{\text{LYP}} + a_c \Delta E_{\text{MP2}},$$

(8)

with two parameters, of which the practical values are given by Grimme [18] as $a_x = 0.53$ and $a_c = 0.27$.

The present method was demonstrated by the illustrative application to the oligoacene test system, C$_{4n+2}$H$_{2n+4}$, shown in Fig. 1. In DC calculations, we adopted C$_4$H$_2$ (or C$_6$H$_2$ for the center, C$_4$H$_4$ for the edges) group depicted in Fig. 1 as a central region and treated two adjacent C$_4$H$_2$ (or C$_6$H$_2$ or C$_4$H$_4$) units as corresponding MP2 buffer region. The SCF calculations were performed in the standard manner, without using the DC scheme. Fig. 2 shows the singlet-triplet energy gap ($E_{\text{triplet}} - E_{\text{singlet}}$) calculated by the UHF and DC-B2PLYP methods with 6-31G** basis set [21]. The experimental values are also shown for $n = 3$ and 5. Although the experimental singlet-triplet gap decreases as the system enlarges, the UHF method exhibits a completely opposite behavior. This tendency was fairly improved by taking the MP2-type correlation expression into account by using the DC-UB2PLYP method.

![Fig. 1. Structure of oligoacene test system C$_{4n+2}$H$_{2n+4}$. The dashed lines separate the central region.](image1)

![Fig. 2. The system-size dependence of the singlet-triplet energy gap of oligoacene C$_{4n+2}$H$_{2n+4}$ calculated by the HF and DC-B2PLYP methods with 6-31G** basis set. Experimental values from Refs. 22 and 23 are shown together.](image2)

### 2.2. Analytical gradient method

The second topic is about the energy gradient method, which is required for the geometry optimizations and molecular dynamics simulations. The energy gradient expression for the DC-HF method was previously proposed.
by Yang and Lee (YL) [3] on the analogy with the standard HF energy gradient expression as:

$$\frac{\partial E^{\text{DC}}}{\partial Q} = \text{Tr} \left[ P^{\text{DC}} \frac{\partial H^{\text{core}}}{\partial Q} \right] + \sum_{\mu \nu \lambda \sigma} P^{\text{DC}}_{\mu \nu \lambda} P^{\text{DC}}_{\lambda \sigma} \left( \frac{1}{2} \left\langle \psi \left| \sigma \lambda \right| \psi \right\rangle - \frac{1}{4} \left\langle \psi \left| \nu \lambda \right| \psi \right\rangle \right) - \text{Tr} \left[ W^{\text{DC}} \frac{\partial S}{\partial Q} \right]. \quad (9)$$

Here, $H^{\text{core}}$ is the core Hamiltonian matrix and $W^{\text{DC}}$ is the energy-weighted density matrix evaluated in the DC manner:

$$W^{\text{DC}}_{\mu \nu} = 2 \sum_{\alpha} p_{\mu \nu}^{\alpha} \sum_{q} f_{\alpha} \left( e_{\alpha}^{\mu} - e_{\alpha}^{\nu} \right) e_{q}^{\alpha} e_{q}^{\alpha} C_{\mu \nu}^{\alpha \alpha}.$$  \quad (10)

We here emphasize that Eq. (9) is only a DC-like approximation of the standard HF energy gradient. The proper starting point of the DC-HF energy gradient is the direct differentiation of the DC-HF energy. In this point of view, we have proposed a novel expression for the DC-HF energy gradient as [17]:

$$\frac{\partial E^{\text{DC}}}{\partial Q} = \text{Tr} \left[ P^{\text{DC}} \frac{\partial H^{\text{core}}}{\partial Q} \right] + \sum_{\mu \nu \lambda \sigma} P^{\text{DC}}_{\mu \nu \lambda} P^{\text{DC}}_{\lambda \sigma} \left( \frac{1}{2} \left\langle \psi \left| \sigma \lambda \right| \psi \right\rangle - \frac{1}{4} \left\langle \psi \left| \nu \lambda \right| \psi \right\rangle \right) - \frac{1}{2} \text{Tr} \left[ \frac{\partial S}{\partial Q} \sum_{\alpha} X^{\alpha} \right], \quad (11)$$

where

$$X^{\alpha} = W^{\alpha} \left[ \delta \left(L(\alpha) \gamma S(\alpha)\right) P \delta \left(S(\alpha) \gamma L(\alpha)\right) \right]. \quad (12)$$

The superscript represents the submatrix with $L(\alpha)$ being the set of basis functions in the central or buffer region of the subsystem $\alpha$.

By numerical assessments of the DC-HF energy gradient in the geometry optimization, it was confirmed that the present method [Eq. (11)] reproduces the structures obtained by the standard HF better than the YL method [Eq. (9)] does [17]. We further tested the method in the ab initio molecular dynamics (AIMD) simulation of a 50 water cluster system at HF/6-31G level of theory with the NVE ensemble. In DC calculations, we adopted one water molecule as a central region and treated the union of the spherical regions centered at the atoms in the central region with radius $r_b$ as corresponding buffer region. Time propagation was performed by the velocity Verlet method with the time step of 0.5 fs. Fig. 3 shows the time evolution of the total energy, which should be kept constant with the NVE ensemble. The energy fluctuation decreases as the adopted buffer size becomes large, and it becomes 0.25 mHartree for $r_b = 7$ Å in this simulation, which is quite close to 0.24 mHartree for the conventional calculation. The energy variations of the present method are 3.4 and 0.64 mHartree for $r_b = 5$ and 6 Å that are smaller than those of the YL method, being 5.0 and 0.89 mHartree, respectively.

![Fig. 3. The time evolution of the total energy in the AIMD simulation of a 50 water cluster system at HF/6-31G level with the NVE ensemble.](image-url)
3. Summary

The capability of the present DC code in GAMESS program package is summarized in Table 1. In addition to the energy and gradient calculations listed in Table 1, frequency-dependent polarizability obtained by the coupled perturbed equations is available in HF/DFT level of theory [24]. Furthermore, the DC energy is also applicable to the static (hyper)polarizability calculations with the finite electric field method [25]. The acceleration of the SCF convergence has been examined by means of direct inversion in the iterative subspace (DIIS) [4] and fractional occupation number (FON) [26] techniques. The DC-DIIS and DC-FON are available in the latest version of the GAMESS package.

We hope that the present implementation is sufficiently valuable for the practical calculations of functional materials. However, we are continuously developing the fundamental theory and corresponding program code to improve the computational feasibility. The two-level hierarchical parallelization scheme [27] is being investigated in order to making possible DC-MP2 calculations in massively parallel computers such as upcoming next-generation supercomputer “K”.

Table 1. Capability of the DC code in GAMESS program package.

| Level of theory               | Closed-shell | Open-shell |
|------------------------------|--------------|------------|
|                              | Energy       | Gradient   | Energy       | Gradient   |
| HF                           | ✓            | ✓          | ✓            | ✓          |
| DFT (LDA, GGA, meta-GGA, hyper-GGA) | ✓            | ✓          | ✓            | ✓          |
| MP2                          | ✓            | in progress| ✓            | ✓          |
| CCSD                         | ✓            |            |              |            |
| CCSD(T)                      | ✓            |            |              |            |

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