Automatic fragmentation in the divide and conquer quantum chemical calculations with the energy error estimation

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Keywords: Hartree-Fock (HF) calculation; Second-order Møller-Plesset (MP2) calculation; Linear-scaling electronic structure calculation

Many fragmentation-based electronic structure methods such as the divide-and-conquer (DC) method[1] have been developed to reduce the computational time for calculations of large-scale systems. However, these methods result in introducing the energy errors associated with the fragmentation. In addition, most of these methods use parameters other than energy in the control of the energy errors. In this study, we report automatic error control schemes in the DC-HF and DC-MP2 calculations with the estimation of the energy variation associated with the fragment change, which is controlled with the buffer region in case of the DC method.

In the DC-HF calculation, we introduce the two-layered buffer region for each disjoint fragment (central region). The energy variation by transferring each atom in the outer buffer region into the inner buffer region can be estimated by means of the subsystem density matrix.[2] As for the DC-MP2 calculation, we derived the upper bound of the electron correlation energy contribution for each atom in the buffer regions based on the atomic orbital Laplace MP2 method and Schwarz inequality.[3] With these estimated energy as the criterion, the appropriate buffer region can be automatically determined for each of the DC-HF and DC-MP2 methods.

The automated DC-MP2 calculation was performed for 100 water molecules (Table). From the average fragment size, the present method can effectively aid the selection of the appropriate buffer region for each subsystem in the DC-HF and DC-MP2 calculations. Consequently, the energy error was almost constant in any initial conditions.

Table. Initial DC-HF buffer-size (r_b^{in} and r_b^{out}) dependence of the automated DC-MP2 correlation energy ($E_{corr}^{(2)}$) and the major axis radius ($\langle l_{HF}^\alpha \rangle$ and $\langle l_{corr}^\alpha \rangle$) for 100 water cluster system.

r_b^{in} /Å	r_b^{out} /Å	E_{HF}/E_h	$E_{corr}^{(2)}/E_h$	(Diff.)/μE_h atom^{-1}	$\langle l_{HF}^\alpha \rangle$ /Å	$\langle l_{corr}^\alpha \rangle$ /Å
3.5	4.5	−7601.504443	−19.105142	(+8.37)	7.233	6.564
4.0	5.0	−7601.504613	−19.105141	(+8.37)	7.238	6.538
4.5	5.5	−7601.504342	−19.105031	(+8.74)	7.161	6.522
5.0	6.0	−7601.504417	−19.105000	(+8.84)	7.161	6.480
5.5	6.5	−7601.504467	−19.105185	(+8.23)	7.000	6.427
Standard MP2		−7601.504673	−19.107652			

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