Advanced Electronic Structure Theory in Quantum Chemistry

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

YANAI, Takeshi	Associate Professor
KURASHIGE, Yuki	Assistant Professor
MIZUKAMI, Wataru	Graduate Student
YAMADA, Mariko	Secretary

Aiming at predictive computational modelings of molecular electronic structures with *ab initio* quantum chemistry calculations, our scientific exploration is to establish a cutting-edge theoretical methodology that allows one to compute accurately and efficiently the complex electronic structures where the substantial multireference character in the wave functions has to be handled for the qualitative and quantitative descriptions. Our resultant works to be reported here are (1) to develop a new type of the multireference correlation model named Canonical Transformation (CT) theory, which can efficiently describe short-range dynamic correlation on top of the multi-configurational staring wave function, and (2) to construct the extensive complete active space self-consistent field (CASSCF) method combined with *ab initio* density matrix renormalization group (DMRG) method for making unprecedentedly larger active spaces available for the CASSCF calculations. These two pivotal developments are tailored to eventually be incorporated for solving large-scale multireference electronic structure problems.

1. Large-Scale Complete Active Space Self-Consistent Field (CASSCF) with *ab initio* Density Matrix Renormalization Group (DMRG): “DMRG-CASSCF”[1]

To perform the large-scale multireference calculations with CT or other multireference methods, the extensively active-spaced reference wave functions where a large number of active electrons are highly (or fully) correlated within the selected active orbitals must be found. The CASSCF method provides the most desirable, optimal reference wave functions, in which the static correlations are effectively captured with the relaxed active orbitals that are optimized self-consistently by energy minimization at a high computational cost. We have developed the large-scale CASSCF method by implementing orbital optimization in the extant DMRG implementation to further allow the self-consistent improvement of the active orbitals, as is done in the standard CASSCF calculations. By virtue of the compact nature of the DMRG wavefunction, this now enables us to handle unprecedentedly larger active space than are possible with the traditional CASSCF. The further feasibility comes concomitantly with a new development of the parallelized orbital optimization allowing for high-quality basis representations of the orbitals. We have named the resulting method DMRG-CASSCF (Figure 1).

Figure 1. Schematic sketch of DMRG-CASSCF implementation. CI and MO coefficients are determined with the alternating two-step algorithm. The new development has realized the efficient computation of 1-, 2-RDMs of DMRG wavefunction, taking advantage of the compact structure of DMRG ansatz.

As applications, we have used our DMRG-CASSCF method to study the low-lying excitations of polyenes from C_8H_{10} to $C_{24}H_{26}$ (11 conjugated bonds) as well as light-harvesting pigment, β-carotene (10 conjugated bonds) with up to a CAS (24e,24o) of full π valences (Figure 2–3). The

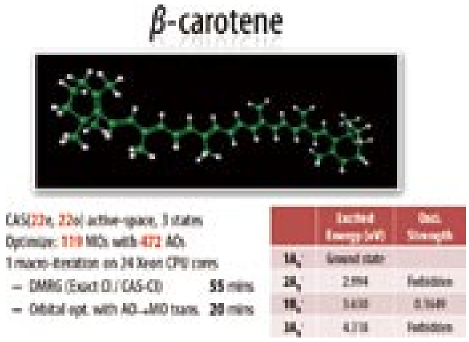


Figure 2. Details of the DMRG-CASSCF calculation for β-carotene along with excitation energies of its three dark states.

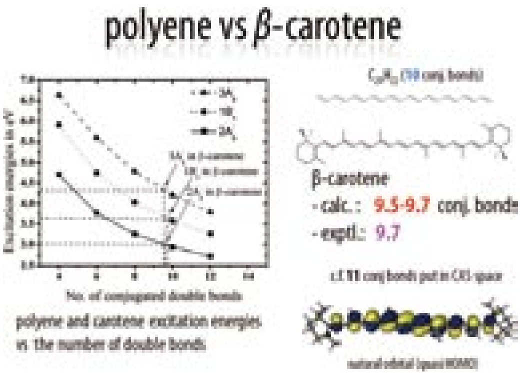
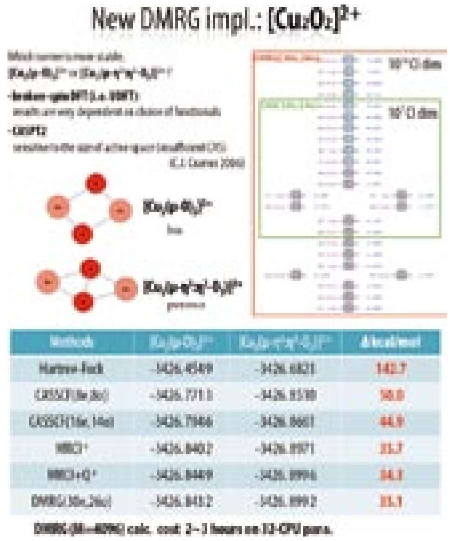


Figure 3. Carotene excitation energies of three states are fitted to polyene excitation energies. We estimated an effective conjugation length of beta-carotene to be 9.5–9.7. These numbers are in good agreement with the experimental estimation 9.7.

conjugated π-system in polyenes and substituted species such as β-carotene give rise to an unusual excitation spectrum, with "dark" electronic states lying beneath the optically allowed HOMO-LUMO transition. The electronic structure of these low-lying states lies at the heart of energy transport in system ranging from the conjugated organic semiconductors to the biological centers of light-harvesting and vision. While the relevant active space on these systems clearly consists of the conjugated π-valence orbitals, to the best of our knowledge, previous calculations have used "incomplete" π-valence space which is limited up to CAS (10e,10o) (*i.e.* 5 nominal conjugated bonds).

2. Robust Implementation of *ab initio* DMRG for Transition Metal Molecular Complexes

Our group has started an alternative implementation of *ab initio* DMRG with algorithmic improvements in which we have some new tricks in constructing operators in renormalization and subspacing Hamiltonian. The development is ongoing with a new scheme of computer parallelism for flop- and memory-distributions of DMRG operators. The development is tailored to computationally affordable applications to accurate, robust electronic structure calculations of complex transition-metal complexes, for which the conventional theoretical treatments get in trouble with entangled electronic states inherent to *d* electrons/orbitals. Figure 4 shows the recent achievement in the performances of our DMRG implementation for calculating isomerization energies of $Cu_2O_2^{2+}$ core. Our method recovers a substantial portion of the full correlation energies efficiently from correlating valence *d* electrons of two Cu atoms with other valences of Cu and O atoms on equal footing



Methods			Δ kcal/mol
Hartree-Fock	-3426.4549	-3426.6821	142.7
CASSCF(8e,8o)	-3426.7711	-3426.8530	50.0
CASSCF(16e,14o)	-3426.7946	-3426.8661	44.9
MRCI+	-3426.8402	-3426.8971	35.7
MRCI+Q+	-3426.8449	-3426.8996	34.3
DMRG(30e,26o)	-3426.8432	-3426.8992	35.1

DMRG (M=4096) calc. cost: 2~3 hours on 32-CPU para.

Figure 4. Isomerization energies of $Cu_2O_2^{2+}$ core between bis and peroxo structures by various methods including our new implementation of DMRG. The new, efficient implementation carried out the fully correlated electronic structure calculations.

3. Canonical Transformation (CT) Theory for Efficient Multireference Method[2)]

We have been developing a many-body technique based on canonical transformation (CT) for realizing large-scale multireference calculations for the purpose of attaining the chemical accuracy, for which dynamical correlations are described by using cluster expansion on top of muticonfigurational setting (*e.g.* DMRG-CASSCF). We are working on extending the implementation to the wider applications in terms of tractable size of molecules of target. The ongoing reimplementation fixes some of problems in the extant implementation that relies on infinite computer memory. Figure 5 presents the recent application of CT to the description of an energy curve along the isomerization coordinate between bis and peroxo cores of $Cu_2O_2^{2+}$.

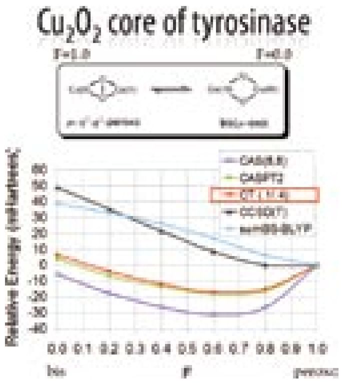


Figure 5. Relative energy curves along the isomerization coordinate between bis and peroxo cores. The difficulty in describing electronic structure of this isomerization arises in maintaining the balanced description of rapidly changing dynamic and static correlation effects and a varying degree of biradical character along the coordinate.

References

1) D. Ghosh, J. Hachmann, T. Yanai and G. K-L. Chan, *J. Chem. Phys.* **128**, 144117 (2008).
2) T. Yanai and G. K-L. Chan, *J. Chem. Phys.* **127**, 104107 (2007).
3) H. Sekino, Y. Maeda, T. Yanai and R. J. Harrison, *J. Chem. Phys.* **129**, 034111 (6 pages) (2008).