Advanced Electronic Structure Theory in Quantum Chemistry

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Education
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Professional Employment
2001 Postdoctoral Fellow, The University of Tokyo
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2005 Postdoctoral Fellow, Cornell University
2007 Associate Professor, Institute for Molecular Science
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Awards
2008 Chemical Physics Letters Most Cited Paper 2003-2007 Award
2009 The Wiley-International Journal of Quantum Chemistry Young Investigator Award
2013 Laureate, International Academy of Quantum Molecular Science
2013 Japan Society of Molecular Science
2017 Pople Medal of Asia-Pacific Conference of Theoretical and Computational Chemistry

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Computational quantum chemistry, that is, practicing quantum chemical theory using computers, is now considered to be a powerful means to provide detailed analysis of chemical phenomena. The focus of our group is to develop methods and algorithms of molecular electronic structure calculations, which are capable of supplying electronic-level interpretation and reliable prediction of chemical characters, reactivity, energetics, and spectroscopic properties of molecular systems. Also, we are interested in applying the methods to challenging chemical systems. Recently, we have developed advanced multireference methods to describe highly-correlated many-electron wavefunction, which cannot be qualitatively accounted for with mean-field or one-electron theory (*e.g.*, density functional theory). The multireference wavefunction need be represented with a quantum superposition of multiple electron configurations; however, this gives rise to a high computational expense because the degree of the superposition is in general exponentially dependent on the system size. We approach the multireference problems using the density matrix renormalization group (DMRG), which is originally a method of condensed matter physics to solve strong correlation phenomena in physical models. We developed an efficient implementation for adapting DMRG to quantum chemical calculation, in which the DMRG is exploited to describe static correlation in combination with the complete active space (CAS) model. Our DMRG-based methods have shown to be capable of handling very large correlation space, which far exceeds the limitation of conventional methods. We have further introduced a scheme to additively account for dynamic correlation on top of active-space DMRG wavefunction. Using these methods, we carried out chemical applications to multireference electronic systems, ranging from organic material molecules, such as radicals of graphene nanoribbons, to transition metal complexes, such as tetranuclear manganese cluster.

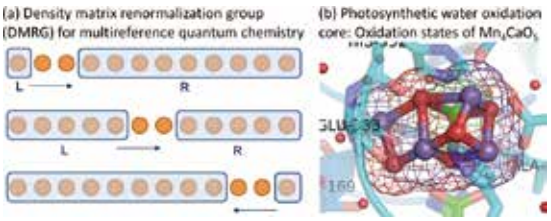

Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

Selected Publications

- Y. Kurashige and T. Yanai, "High-Performance *Ab Initio* Density Matrix Renormalization Group Method: Applicability to Large-Scale Multireference Problems for Metal Compounds," *J. Chem. Phys.* **130**, 234114 (21 pages) (2009).
- W. Mizukami, Y. Kurashige and T. Yanai, "More π Electrons Make a Difference: Emergence of Many Radicals on Graphene Nanoribbons Studied by *Ab Initio* DMRG Theory," *J. Chem. Theory Comput.* **9**, 401–407 (2013).
- Y. Kurashige, G. K-L. Chan and T. Yanai, "Entangled Quantum Electronic Wavefunctions of the Mn_4CaO_5 Cluster in Photosystem II," *Nat. Chem.* **5**, 660–666 (2013).

1. Multistate Complete Active Space Second Order Perturbation Theory Based on Density Matrix Renormalization Group Reference States[1)]

We present the development of the multistate multireference second-order perturbation theory (CASPT2) with multi-root references, which are described using the density matrix renormalization group (DMRG) method to handle a large active space. The multistate first-order wave functions are expanded into the internally contracted (IC) basis of the single-state single-reference (SS-SR) scheme, which is shown to be the most feasible variant to use DMRG references. The feasibility of the SS-SR scheme comes from two factors: First, it formally does not require the fourth-order transition reduced density matrix (TRDM); and second, the computational complexity scales linearly with the number of the reference states. The extended multistate (XMS) treatment is further incorporated, giving suited treatment of the zeroth-order Hamiltonian despite the fact that the SS-SR based IC basis is not invariant with respect the XMS rotation. In addition, the state-specific fourth-order reduced density matrix (RDM) is eliminated in an approximate fashion using the cumulant reconstruction formula, as also done in the previous state-specific DMRG-cu(4)-CASPT2 approach. The resultant method, referred to as DMRG-cu(4)-XMS-CASPT2, uses the RDMs and TRDMs of up to third-order provided by the DMRG calculation (**Figure 2**). The multistate potential energy curves of the photoisomerization of diarylethene derivatives with CAS(26e,24o) are presented to illustrate the applicability of our theoretical approach (**Figure 3**).

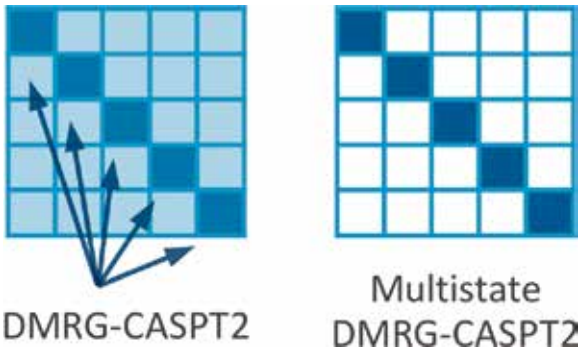

Figure 2. Development of multistate multireference perturbation theory with density matrix renormalization group references.

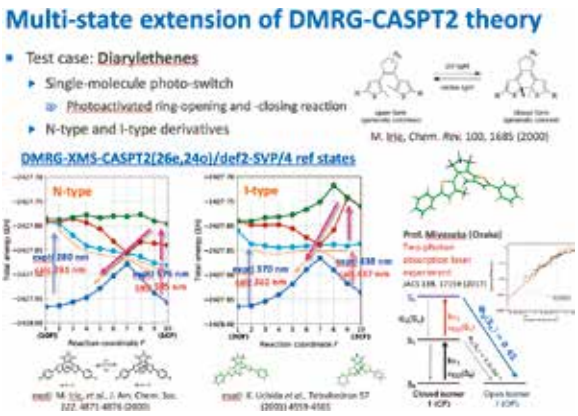

Figure 3. Application of DMRG-XMS-CASPT2 theory for studying potential energy curves of S_0–S_3 states of two types of diarylethene derivatives with use of large active space, CAS(26e,24o), considering four reference states.

2. Robust and Efficient Relativistic Complete Active Space Self-Consistent Field[2)]

We report a highly efficient algorithm using density fitting for the relativistic complete active space self-consistent field (CASSCF) method, which is as efficient as, but significantly more stable than, the algorithm previously reported. Our algorithm is based on the second-order orbital update scheme with an iterative augmented Hessian procedure, in which the density-fitted orbital Hessian is directly contracted to the trial vectors. Using this scheme, each microiteration is made less time consuming than one Dirac–Hartree–Fock iteration, while macroiteration converges quadratically. In addition, we show that the CASSCF calculations with the Dirac–Gaunt and Dirac–Breit interactions can be sped up by means of approximate orbital Hessians computed with the Dirac–Coulomb interaction. It is demonstrated that our algorithm can also be applied to systems under an external magnetic field, for which all of the molecular integrals are computed using gauge-including atomic orbitals.

References

1) T. Yanai, M. Saitow, X.-G. Xiong, Y. Kurashige, J. Chalupský, S. Guo and S. Sharma, *J. Chem. Theory Comput.* **13**, 4829–4840 (2017).

2) R. D. Reynolds, T. Yanai and T. Shiozaki, *J. Chem. Phys.* **149**, 014106 (2018).

Award

SAITOW, Masaaki; 2017 Molecular Physics Early Career Researcher Prize.