

Advanced Electronic Structure Theory in Quantum Chemistry

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Education

1997 B.S. The University of Tokyo
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Professional Employment

2001 Postdoctoral Fellow, The University of Tokyo
2002 Postdoctoral Fellow, Pacific Northwest National Laboratory
2002 Postdoctoral Fellow, Oak Ridge National Laboratory
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
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Electronic Structure Theory, Quantum Chemistry, Computational Chemistry

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,

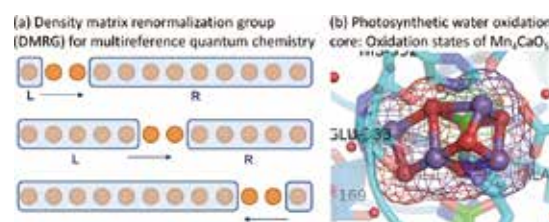


Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

tion, 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.

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 Nano-

ribbons 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. Fully Internally Contracted Multireference Configuration Interaction Theory Using Density Matrix Renormalization Group

We present an extended implementation of the multi-reference configuration interaction (MRCI) method combined with the quantum-chemical density matrix renormalization group (DMRG). In the previous study, we introduced the combined theory, referred to as DMRG-MRCI, as a method to calculate high-level dynamic electron correlation on top of the DMRG wavefunction that accounts for active-space (or strong) correlation using a large number of active orbitals. The previous implementation achieved the MRCI calculations with the active space (24e,24o), which are deemed the record largest, whereas the inherent $O(N^9)$ complexity of computation was found a hindrance to use further large active space. In this study, an extended optimization of the tensor contractions is developed by explicitly incorporating the rank reduction of the decomposed form of the cumulant-approximated tensors into the factorization. It reduces the computational scaling (to $O(N^8)$) as well as the cache-miss penalty. The new DMRG-MRCI implementation is applied to the determination of the stability of the iron(IV)-oxo porphyrin relative to the iron(V) electronic isomer (electromer) using the active space (29e,29o) (including four second d-shell orbitals of iron) with triple- z -quality atomic orbital basis sets. The DMRG-MRCI model is shown to favor the triradicaloid iron(IV)-oxo state as the lowest-energy state and characterize the iron(V) electromer as thermally inaccessible, supporting the earlier experimental and density functional studies. This conflicts with the previous MR calculations using the restricted active space second-order perturbation theory with the similar-size active space (29e,28o) reported by Pierloot *et al.* [M. Radon, E. Broclawik, and K. Pierloot, *J. Chem. Theory Comput.* **7**, 898 (2011)], showing that the hypothetical iron(V) state indicated by recent laser flash photolysis (LFP) studies is likely thermally accessible because of its underestimated relative energy.

2. Scalar Relativistic Calculations of Hyperfine Coupling Constants Using *Ab Initio* DMRG⁵⁾

We have developed a new computational scheme for high-accuracy prediction of the isotropic hyperfine coupling constant (HFCC) of heavy molecules accounting for the high-level electron correlation effects as well as the scalar-relativistic effects. For electron correlation, we employed the *ab initio* DMRG method in conjunction with a complete active space model. The orbital-optimization procedure was employed to obtain the optimized orbitals required for accurately determining the isotropic HFCC. For the scalar-relativistic effects, we initially derived and implemented the Douglas-Kroll-Hess

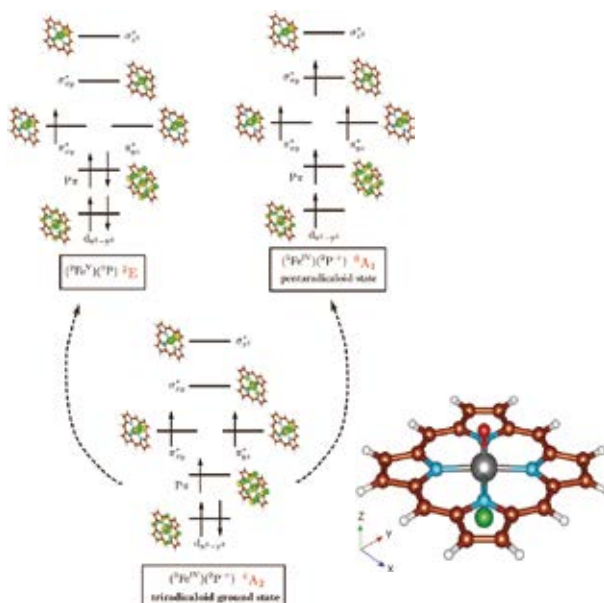


Figure 2. Electronic isomers of FeO(P)Cl molecule and their electronic configurations 4A_2 is a formal ground state; however, recent LFP analysis suggests the presence of the stable 6A_1 state.

hyperfine coupling operators up to the third order by using the direct transformation scheme. A set of $4d$ transition metal radicals consisting of Ag atom, PdH, and RhH₂ were chosen as test cases. Good agreement between the isotropic HFCC values obtained from DMRG/DKH3 and experiment was archived.

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- 6) Y. Ishikawa, S. Kimura, K. Takase, K. Yamamoto, Y. Kurashige, T. Yanai and T. Murahashi, *Angew. Chem., Int. Ed.* **54**, 2482–2486 (2015).
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- 8) T. Yanai, G. I. Fann, R. J. Harrison and G. Beylkin, *Phys. Chem. Chem. Phys.* (12 pages) (2015). DOI: 10.1039/c4cp05821f
- 9) S. Horiuchi, Y. Tachibana, K. Yamamoto, S. Kawamata, K. Takase, T. Matsutani, K. Masai, Y. Kurashige, T. Yanai and T. Murahashi, *Nat. Commun.* **6**, 6742 (8 pages) (2015).

Award

KURASHIGE, Yuki; The Chemical Society of Japan Award for Young Chemists 2014.