Advanced Electronic Structure Theory in Quantum Chemistry

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Education

1997	B.S. The University of Tokyo
2001	Ph.D. The University of Tokyo

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 Associate Professor, The Graduate University for Advanced Studies

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

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Keywords 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, 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.

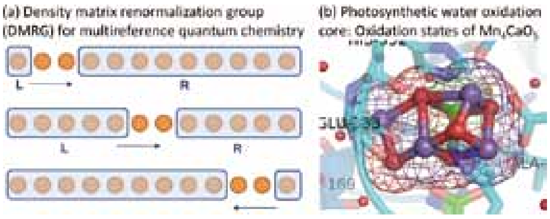

Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

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. Radical O–O Coupling Reaction in Diferrate-Mediated Water Oxidation Studied with Multireference Wave Function Theory[1)]

Recently, the water oxidation catalyzed by potassium ferrate K_2FeO_4 was investigated on the basis of experimental kinetic isotope effect analysis assisted by density functional calculations, revealing the intramolecular oxo-coupling mechanism within a di-iron(VI) intermediate, or diferrate [Sarma *et. al.*, *J. Am. Chem. Soc.* **134**, 15371 (2012)]. Here, we reported a detailed examination of this diferrate-mediated O–O bond formation using scalable multireference electronic structure theory. High-dimensional correlated many-electron wave functions beyond one-electron picture were computed with *ab initio* DMRG method along the O–O bond formation pathway. The necessity of using large active space arises from the description of complex electronic interactions and varying redox states both associated with two-center antiferromagnetic multivalent iron–oxo coupling. Dynamic correlation effects on top of the active space DMRG wave functions were additively accounted for by complete active space second-order perturbation (CASPT2) and multireference configuration interaction (MRCI) based methods, which were recently introduced by our group. These multireference methods were capable of handling the double shell effects in the extended active space treatment. The calculations with CAS(36e,32o), which is far over conventional limitation, provide a quantitatively reliable prediction of potential energy profiles and confirmed the viability of direct oxo coupling. (**Figure 2**).

2. Toward Reliable Prediction of Hyperfine Coupling Constants Using *Ab Initio* Density Matrix Renormalization Group Method[2)]

The DMRG method was used in conjunction with the CASCI and CASSCF methods to evaluate hyperfine coupling constants (HFCCs) for a series of diatomic $^2\Sigma$ radicals (BO, CO^+, CN, and AlO) and vinyl (C_2H_3) radical. The electron correlation effects on the computed HFCC values were systematically investigated using various levels of active space, which were increasingly extended from single valence space to large-size model space entailing double valence and at least single polarization shells. In addition, the core correlation was treated by including the core orbitals in active space. Reasonably accurate results were obtained by the DMRG-CASSCF method involving orbital optimization, while DMRG-CASCI calculations with Hartree-Fock orbitals provided poor agreement of the HFCCs with the experimental values. To achieve further insights into the accuracy of HFCC calculations, the orbital contributions to the total spin density were analyzed at a given nucleus, which is directly related to the FC term and is numerically sensitive to the level of correlation treatment and basis sets. This work serves as the first study on the performance of the *ab initio* DMRG method for HFCC prediction.

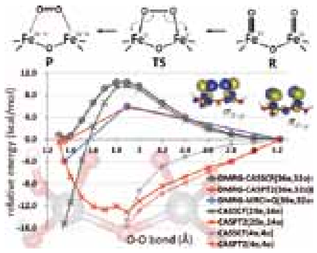

Figure 2. Diferrate-mediated O–O bond formation was studied using *ab initio* DMRG theory with large-size active space CAS(36e,32o) in conjunction with dynamic correlation correction.

3. Flexible Nuclear Screening Approximation to the Two-Electron Spin–Orbit Coupling Based on *Ab Initio* Parameterization[3)]

The derivation, implementation, and validation of a new approximation to the two-electron spin–orbit coupling (SOC) terms was reported. The approximation, referred to as flexible nuclear screening spin–orbit (FNSSO), is based on the effective one-electron spin–orbit operator and accounts for two-electron SOC effects by screening nuclear charges. A highly flexible scheme for the nuclear screening is developed, mainly using parameterization based on *ab initio* atomic SOC calculations. Tabulated screening parameters are provided for contracted and primitive Gaussian-type basis functions of the ANO-RCC basis set for elements from H to Cm. A model to correct for the effect of spin–orbit splitting of transition metal *d* orbitals on their SOC matrix elements was introduced. The method is applied to a representative set of molecules, and compared to exact treatment and other approaches at the same level of relativistic theory. The calculated SOC matrix elements are in very good agreement with their "exact" values; deviation below 1% is observed on average.

References

1) Y. Kurashige, M. Saitow, J. Chalupský and T. Yanai, *Phys. Chem. Chem. Phys.* **16**, 11988–11999 (2014).
2) L. N. Tran, Y. Kurashige and T. Yanai, *J. Chem. Theory Comput.* **10**, 1953–1967 (2014).
3) J. Chalupský and T. Yanai, *J. Chem. Phys.* **139**, 204106 (14 pages) (2013).
4) F. Liu, Y. Kurashige, T. Yanai and K. Morokuma, *J. Chem. Theory Comput.* **9**, 4462–4469 (2013).
5) Y. Kurashige, *Mol. Phys.* **112**, 1485–1494 (2014).
6) S. Sharma, T. Yanai, G. H. Booth, C. J. Umrigar and G. K.-L. Chan, *J. Chem. Phys.* **140**, 104112 (8 pages) (2014).
7) T. V. Harris, Y. Kurashige, T. Yanai and K. Morokuma, *J. Chem. Phys.* **140**, 054303 (10 pages) (2014).

Awards

YANAI, Takeshi; Laureate, International Academy of Quantum Molecular Science 2013.
YANAI, Takeshi; Young Scientist Awards of the Japan Society for Molecular Science 2013.
KURASHIGE, Yuki; MORINO Foundation for Molecular Science 2014.