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
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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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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.

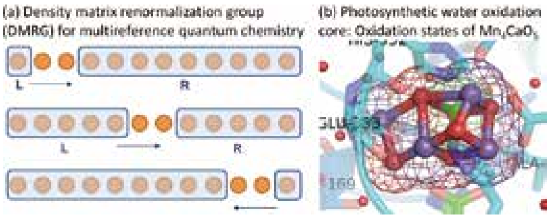


Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

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).

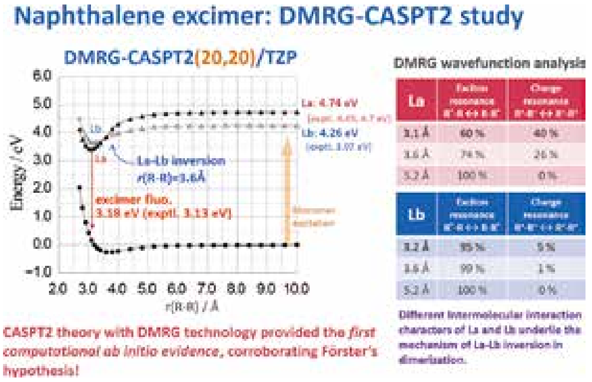
1. Computational Evidence of Inversion of ^1L_a and ^1L_b-Derived Excited States in Naphthalene Excimer Formation from Highly-Correlated *ab initio* Multireference Theory[2)]

The naphthalene molecule has two important lowest-lying singlet excited states, denoted ^1L_a and ^1L_b. Association of the excited and ground state monomers yields a metastable excited dimer (*excimer*), which emits characteristic fluorescence. Here, we report a first computational result based on *ab initio* theory to corroborate that the naphthalene excimer fluorescence is ^1L_a parentage, resulting from inversion of ^1L_a and ^1L_b-derived dimer states. This inversion was hypothesized by earlier experimental studies; however, it has not been confirmed rigorously. In this study, the advanced multireference (MR) theory based on density matrix renormalization group that enables using unprecedented large-size active space for describing significant electron correlation effects is used to provide accurate potential energy curves (PECs) of the excited states. The results evidenced the inversion of the PECs and accurately predicted transition energies for excimer fluorescence and monomer absorption. Traditional MR calculations with smaller active spaces and single-reference theory calculations exhibit serious inconsistencies with experimental observations.

The excimer formation is driven by the strong ^1L_a's attractive intermolecular interaction arising from a mixing of excition resonance (ER) and charge resonance (CR) configurations. At large distance r(R–R) = 5.2 Å, $^1L_a{}^-$ and $^1L_b{}^-$ states are both characterized by near 100% ER. In $^1L_a{}^-$, the CR character rises up to 40% for the excimer formation, while it remains negligible in $^1L_b{}^-$. This near CR-free character in $^1L_b{}^-$ is an interesting finding; the previous semi-empirical approaches were unable to unveil it. Since the transition dipole moment of the monomer ^1L_b is much smaller than that of ^1L_a, the attractive interaction in $^1L_b{}^-$ driven by ER alone should be far weaker than that in $^1L_a{}^-$. In the presence of the transition dipole–transition dipole interaction, the attractive interaction in $^1L_a{}^-$ is further pronounced by the growth of its CR character, as modeled by the semi-empirical approach. These imbalanced intermolecular interactions underlie the mechanism of the inversion of the two excitation levels.

2. Theoretical Investigation into Pentanuclear Iron Catalyst Designed for Water Oxidation[3)]

Quantum chemistry calculations were performed on the pentanuclear iron complex and its reaction intermediates using density functional theory (DFT). The catalyst based on the complex was recently developed by Masaoka group; it was revealed that it here has a remarkable ability to catalyze water oxidization with significant efficiency and robustness. We first examined the viability of water attack reaction. Potential energy surface scan calculations were carried out to derive a reaction pathway of the insertion of a single water to the cluster. Our computational model showed that the coordination of water to activation iron site occurs with activation barrier of 14 kcal/mol. Next, we assume that the reaction proceeds to the coordination of another water and sequential or simultaneous deprotonation, affording cofacial Fe=O radical units. It was found that these top and bottom iron sites play a role as oxidants that withdraw two electrons from water-coordinated activation iron sites during deprotonation; so, intramolecular electron rearrangement takes place between central sites and up-down sites, and they assist generation of reactive high-valence iron-oxo species. Importantly, the number of electrons are conserved in the step. This system was found a mixed valence system involving three kinds of valence, Fe^{II}, Fe^{III}, and Fe^{IV}, simultaneously. Such remarkable redox flexibility is perhaps responsible for high efficiency of catalytic core. In addition, our computational investigation indicated that the O–O bond formation proceeds from the mixed-valence $Fe^{II}_2Fe^{III}(Fe^{IV}{=}O)_2$ intermediate with a reaction barrier of less than 10 kcal mol^{-1}.



La	Exciton resonance	Charge resonance
3.1 Å	60 %	40 %
3.6 Å	74 %	26 %
5.2 Å	100 %	0 %

Lb	Exciton resonance	Charge resonance
3.2 Å	95 %	5 %
3.6 Å	99 %	1 %
5.2 Å	100 %	0 %

CASPT2 theory with DMRG technology provided the *first computational ab initio evidence*, corroborating Förster's hypothesis!

Different intermolecular interaction characters of La and Lb underlie the mechanism of La-Lb inversion in dimerization.

Figure 2. The potential energies of naphthalene dimer of ground, La and Lb excited states as a function of intermolecular distance. DMRG wavefunction analysis showing the weights of exciton and charge resonance characters of the DMRG-CASSCF wavefunction.

References

1) T. Yanai, Y. Kurashige, W. Mizukami, J. Chalupský, T. N. Lan and M. Saitow, *Int. J. Quantum Chem.* **115**, 283–299 (2015).
2) S. Shirai, Y. Kurashige and T. Yanai, *J. Chem. Theory Comput.* **12**, 2366–2372 (2016).
3) M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, M. Yoshida, K. Yoneda, S. Kawata and S. Masaoka, *Nature* **530**, 465–468 (2016).

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