

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
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
2017 Pople Medal of Asia-Pacific Conference of Theoretical and Computational Chemistry

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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,

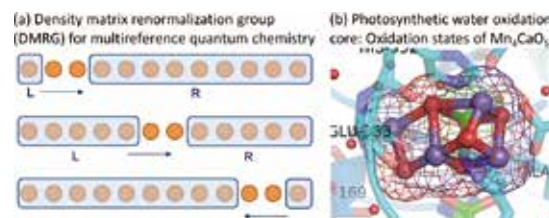


Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

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. Direct Observation of the Ultrafast Evolution of Open-Shell Biradical in Photochromic Radical Dimer¹⁾

Delocalized biradicals have been extensively studied because of fundamental interests to singlet biradicals and several potential applications such as to two-photon absorption materials. However, many of the biradical studies only focus on the static properties of the rigid molecular structures. It is expected that the biradical properties of the delocalized biradicals are sensitive to the subtle changes of the molecular structures and their local environments. Therefore, the studies of the dynamic properties of the system will give further insight into stable radical chemistry. In this study, we directly probe the ultrafast dynamics of the delocalized biradical of a photochromic radical dimer, pentaarylbimidazole (PABI), by time-resolved visible and infrared spectroscopies and quantum chemical calculations with the extended multistate complete active space second-order perturbation theory (XMS-CASPT2). While the photogenerated transient species was considered to be a single species of the biradical, the present ultrafast spectroscopic study revealed the existence of two transient isomers differing in the contributions of biradical character. The origin of the two metastable isomers is most probably due to the substantial van der Waals interaction between the phenyl rings substituted at the imidazole rings. Unraveling the temporal evolution of the biradical contribution will stimulate to explore novel delocalized biradicals and to develop biradical-based photofunctional materials utilizing the dynamic properties (Figure 2).

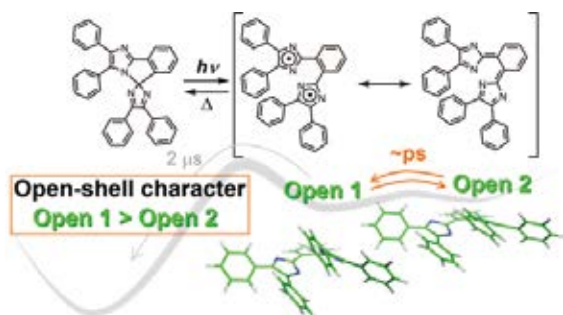


Figure 2. Quantum chemical calculations with XMS-CASPT2 method were performed on PABI in order to illuminate molecular- and electronic-level details of its photochromic ring opening and closing reaction.

2. Projector Augmented Wave Method Incorporated into Gauss-Type Atomic Orbital Based Density Functional Theory²⁾

The Projector Augmented Wave (PAW) method developed by Blöchl is well recognized as an efficient, accurate

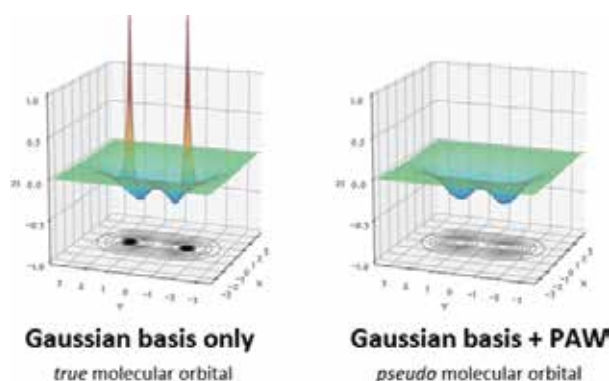


Figure 3. Plots of exact and pseudo molecular orbitals determined for the F_2 molecule with Gauss-type atomic basis functions without and with the PAW pseudopotential treatment.

pseudopotential approach in solid-state density functional theory (DFT) calculations with the plane-wave basis. Here we present an approach to incorporate the PAW method into the Gauss-type function (GTF) based DFT implementation, which is widely used for molecular quantum chemistry calculations. The nodal and high-exponent GTF components of valence molecular orbitals (MOs) are removed or pseudized by the ultrasoft PAW treatment, while there is elaborate transparency to construct an accurate and well-controlled pseudopotential from all-electron atomic description and to reconstruct an all-electron form of valence MOs from the pseudo MOs. The smoothness of the pseudo MOs should benefit the efficiency of GTF-based DFT calculations in terms of elimination of high-exponent primitive GTFs and reduction of grid points in the numerical quadrature. The processes of the PAW method are divided into basis-independent and -dependent parts. The former is carried out using the previously developed PAW libraries libpaw and atompaw. The present scheme is implemented by incorporating libpaw into the conventional GTF-based DFT solver. The details of the formulations and implementations of GTF-related PAW procedures are presented. The test calculations are shown for illustrating the performance. With the near-complete GTF basis at the cc-pVQZ level, the total energies obtained using our PAW method with suited frozen core treatments converge to those with the conventional all-electron GTF-based method with a rather small absolute error (Figure 3).

References

- 1) Y. Kobayashi, H. Okajima, H. Sotome, T. Yanai, K. Mutoh, Y. Yoneda, Y. Shigeta, A. Sakamoto, H. Miyasaka and J. Abe, *J. Am. Chem. Soc.* **139**, 6382–6389 (2017).
- 2) X.-G. Xiong and T. Yanai, *J. Chem. Theory Comput.* **13**, 3236–3249 (2017).

Award

YANAI, Takeshi; The 2017 Pople Medal of Asia-Pacific Conference of Theoretical and Computational Chemistry.