RESEARCH ACTIVITIES

Advanced Electronic Structure Theory in Quantum Chemistry

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

YANAI, Takeshi   Associate Professor
KURASHIGE, Yuki   Assistant Professor
MIZUKAMI, Wataru   Graduate Student
YAMADA, Mariko   Secretary

Aiming at predictive computational modelings of molecular electronic structures with *ab initio* quantum chemistry calculations, our scientific exploration is to establish a cutting-edge theoretical methodology that allows one to compute accurately and efficiently the complex electronic structures, in which strongly-interacting electrons play a crucial role to characterize the nature of molecules. The complicated electronic structures can be handled accurately with the multi-reference theory, which deals with multiple important electronic configurations on equal footing. However, with the standard multireference methods such as the complete active space self-consistent field (CASSCF), the tractable size of the reference space is limited to small active space because the complexity of the calculations grows exponentially with the reference size. The existing multireference methods are nevertheless usefully applied to chemical theory problems such as exploring chemical reactions of bonding, dissociation and isomerization along the reaction coordinates, electronically excited states, unstable electronic structures of radical systems, and multiple covalent bindings in molecular metal complexes, *etc*. Our resultant works to be reported here are (1) to develop a type of the multireference correlation model named Canonical Transformation (CT) theory, which can efficiently describe short-range dynamic correlation on top of the multi-configurational staring wave function, and (2) to construct the extensive complete active space self-consistent field (CASSCF) method combined with *ab initio* density matrix renormalization group (DMRG) method for making unprecedentedly larger active spaces available for the CASSCF calculations.

1. High-Performance *ab initio* Density Matrix Renormalization Group Method Multireference Application for Metal Compounds[1)]

The density matrix renormalization group (DMRG) algorithm has recently attracted significant attention as a robust quantum chemical approach to multireference electronic structure problems in which a large number of electrons have to be highly correlated in a large-size orbital space. It can be seen as a substitute for the exact diagonalization method that is able to diagonalize large-size Hamiltonian matrices. It comprises only a polynomial number of parameters and computational operations, but is able to involve a full set of the Slater determinants or electronic configurations in the Hilbert space, of which the size nominally scales exponentially with the number of active electrons and orbitals. In this work, we have presented a new efficient and parallelized implementation of the DMRG algorithm that is oriented towards applications for poly-nuclear transition metal compounds. The difficulty in DMRG calculations for these systems lies in the large active space and the non-1D nature of the electron correlation. A straightforward extension of the DMRG algorithm has been proposed with further improvements and aggressive optimizations to allow its application with large multireference active space, which is often demanded for metal compound calculations. Special efficiency is achieved by making better use of sparsity and symmetry in the operator and wavefunction representations. By accomplishing computationally intensive DMRG calculations, the authors have found that a large number of renormalized basis states are required to represent high entanglement of the electron correlation for metal compound applications, and it is crucial to adopt auxiliary perturbative correction to the projected density
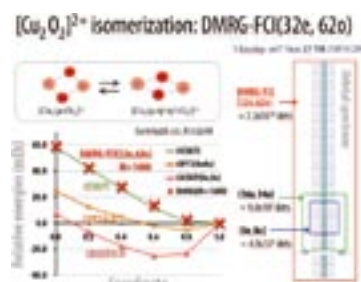

Figure 1. DMRG-FCI application to the potential curve of Cu_2O_2 isomerization, which is recently under hot debate. The behaviors of the single reference calculations and those of the multireference calculations exhibit clear differences. For this problem, we modeled a fairly large orbital space (32e,62o) to execute the DMRG diagonalization with.It has been shown thatDMRG energies nearly overlap with CCSD(T) results..

matrix during the DMRG sweep optimization in order to attain proper convergence to the solution. Potential energy curve calculations for the Cr_2 molecule near the known equilibrium precisely predicted the full configuration interaction (FCI) energies with a correlation space of 24 electrons in 30 orbitals (denoted by (24e,30o)). The energies are demonstrated to be accurate to 0.6 mE_h (the error from the extrapolated best value) when as many as ten thousand renormalized basis states are employed for the left and right DMRG block representations. The relative energy curves for $[Cu_2O_2]^{2+}$ along the isomerization coordinate were obtained from DMRG and other correlated calculations, for which a fairly large orbital space (32e,62o) is modeled as a full correlation space (Figure 1). The DMRG prediction nearly overlaps with the energy curve from the coupled-cluster with singles, doubles and perturbative triples (CCSD(T)) calculations, while the multireference complete active space self-consistent field (CASSCF) calculations with the small reference configuration (8e,8o) are found to overestimate the biradical character of the electronic state of $[Cu_2O_2]^{2+}$, according to the one-electron density matrix analysis.

2. DMRG-CASSCF: Spin States of Poly-Carbene[2]

Posing the multireference problems in quantum chemistry, the complex electronic structures troubling the problems ought to be described by handling multiple electronic configurations, several of which should be equally important in the description. We have recently presented an extensively large-scale CASSCF approach, which is realized by implementing the orbital optimization with the density matrix renormalization group (DMRG) wavefunction (DMRG-CASSCF). By virtue of the compact nature of the DMRG wavefunction, which provides an efficient description of the strongly correlated electronic structures, the DMRG-CASSCF approach enables us to handle much larger active spaces than are possible with the traditional CASSCF
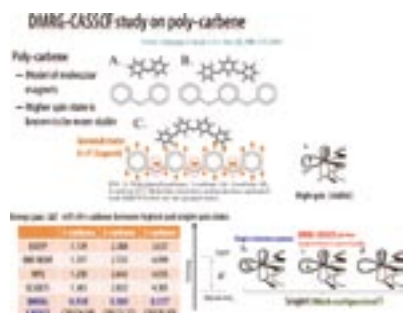
Figure 2. DMRG-CASSCF study of poly(phenyl) carbene. This molecule involves a characteristic electronic structure, and the high-spin state is known to be more stable. For 3-carbene, the septet state is thought to be the most stable spin state where you see there are parallel spins on three carbene sites. The table shows energy gaps of 1,2,3-carbene between highest and singlet spin states. For comparison, reference numbers are computed with several single-reference methods.

algorithm. Using the DMRG-CASSCF method, we investigated the spin states of poly(phenyl)carbenes (Figure 2). These molecules involve a characteristic electronic structure, and the higher-spin states are known to be more stable than the lower-spin states. We examined stability of high-spin state by computing highest and singlet spin states. The table shows energy gaps of 1,2,3-carbene between highest and singlet spin states. For comparison, reference numbers are computed with several single-reference (mean-field + perturbation) methods. In DMRG-CASSCF on 3-carbene, a large CAS(30,30) was used for active space. As expected, all the calculations predicted that high-spin states are more stable than singlet state. However, in terms of the energy gaps, we observed surprisingly large discrepancy between single-reference methods and DMRG-CASSCF. Electronic structure of carbene sites can be represented in sp2 hybridization. Then the high-spin state is described as parallel spins occupying sp2 and p_z orbitals. This description is consistently observed in one-electron density matrix elements of DMRG-CASSCF as well as single determinant wavefunctions. For singlet state, however, as can be seen in the electron density elements, DMRG-CASSCF and single-determinant method chose different configuration. It is found that the single-reference methods describe the lone pair configuration, while DMRG-CASSCF chose this biradical configuration as the stable singlet state. For this reason, DMRG-CASSCF stabilizes the description of the singlet state, and thus the small energy gaps are estimated.

3. Canonical Transformation (CT) Theory for Efficient Multireference Method[3-4]

We have been developing a many-body technique based on canonical transformation (CT) for realizing large-scale multireference calculations for the purpose of attaining the chemical accuracy, for which dynamical correlations are described by using cluster expansion on top of muticonfigurational setting (*e.g.* DMRG-CASSCF). We are working on extending the implementation to the wider applications in terms of tractable size of molecules of target. The ongoing reimplementation fixes some of problems in the extant implementation that relies on infinite computer memory. We have demonstrated the recent application of CT to the description of an energy curve along the isomerization coordinate between bis and peroxo cores of $Cu_2O_2^{2+}$.

References

1) Y. Kurashige and T. Yanai, *J. Chem. Phys.* **130**, 234114 (2009).

2) T. Yanai, Y. Kurashige, D. Ghosh and G. K-L. Chan, *Int. J. Quantum Chem.* **109**, 2178 (2009).

3) E. Neuscamman, T. Yanai and G. K-L. Chan, *J. Chem. Phys.* **130**, 124102 (2009).

4) G. K-L. Chan, J. J. Dorando, D. Ghosh, J. Hachmann, E. Neuscamman, H. Wang and T. Yanai, *Frontiers in Quantum Systems in Chemistry and Physics*, S. Wilson *et al.*, Eds., Springer, **Vol. 18**, pp. 49–64 (2008).