Advanced Electronic Structure Theory in Quantum Chemistry

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

KURASHIGE, Yuki
Assistant Professor

YANAI, Takeshi
Associate Professor

CHALUPSKÝ, Jakub   IMS Fellow   YAMADA, Mariko   Secretary
TRAN, Lan Nguyen   Graduate Student
SAITOW, Masaaki   Graduate Student

Quantum chemistry is a subdiscipline of physical chemistry, and practicing its theory by computer is a powerful approach to chemical theory problems that are rather realistic in terms of size and behaviors. We focus on development of the electronic structure theory that is capable of supplying analytic interpretation of chemical phenomena and is being advanced so that it provides accurate information of experiments a priori. The research is aimed at establishing much better ab initio quantum chemistry methodologies that allow one to describe a wide range of complex electronic structures, which can be found in challenging chemical systems, to a predictive chemical accuracy by exploiting cutting-edge many-body theory and sophisticated computing techniques. The resultant methods are applied for studying molecular science.

Figure 1. Determination of oxidation state of Mn_4CaO_5 cluster in photosystem II from a multireference wavefunction theory based on Denisty Matrix Renormalization Group method.

1. Entangled Quantum Electronic Wave Functions of the Mn_4CaO_5 Cluster in Photosystem II

It is a long-standing goal to understand the reaction mechanisms of catalytic metalloenzymes at an entangled many-electron level, but this is hampered by the exponential complexity of quantum mechanics. Here, by exploiting the special structure of physical quantum states and using the density matrix renormalization group, we compute near-exact many-electron wavefunctions of the Mn_4CaO_5 cluster of photosystem II, with more than 10^{18} quantum degrees of freedom.[1] This is the first treatment of photosystem II beyond the single-electron picture of density functional theory. Our calculations support recent modifications to the structure determined by X-ray crystallography. We further identify multiple low-lying energy surfaces associated with the structural distortion seen using X-ray crystallography, highlighting multistate reactivity in the che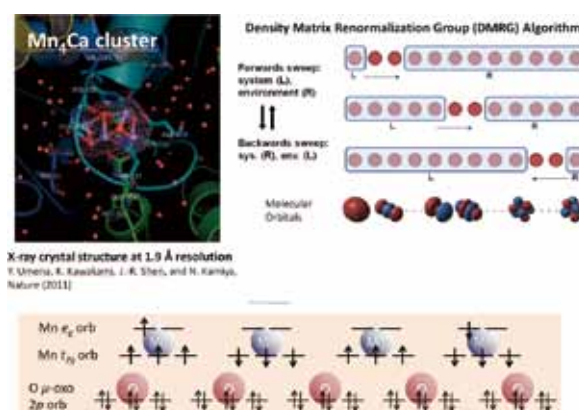mistry of the cluster. Direct determination of Mn spin-projections from our wavefunctions suggests that current candidates that have been recently distinguished using parameterized spin models should be reassessed. Through entanglement maps, we reveal rich information contained in the wavefunctions on bonding changes in the cycle (**Figure 1**).

The capability to obtain a more controlled description of the electronic structure in this complex problem enabled us to more rigorously address structural and electronic questions for the S1 and S2 states. In the S1 case our work confirms the most recent interpretations, and in the S2 state, our direct access to spin states and spin projections suggests that existing candidates, determined on the basis of agreement with EPR data, must be reassessed. The completeness of the many-electron formulation also allowed us to investigate new phenomenology, for example by computing multiple potential-energy surfaces near the S1 state, which highlight non-adiabaticity and multistate reactivity in the OEC. In addition, we

have shown how the information in the many-electron wave-function can be interpreted through its orbital entanglement map, which graphically illustrates the different kinds of chemical bonding and their changes during the Kok cycle. The detailed mechanistic implications of these changes are intriguing and remain an eventual target of study for the future. More broadly, the theoretical methodology we have established is very generally applicable, and opens up the possibility of understanding the electronic structure and, eventually, the chemical mechanism of biological processes at the entangled quantum many-electron level.

2. Correlated One-Body Potential from Second-Order Møller-Plesset Perturbation Theory: Alternative to Orbital-Optimized MP2 Method

The molecular orbitals (MOs) are a key concept in quantum chemistry to interpret the role of electrons in chemical bondings and reactions. They represent the behavior of one electron moving in the effective potential to which Coulomb interactions with many other electrons are averaged out. The effective mean field description is formulated in the Hartree-Fock (HF) theory as a result of using a single determinant as the model wave function in which electron correlation is dismissed in the solution of many-electron Schrödinger equation. In addition to the shapes of MOs, the orbital energies play a central role to characterize molecular electronic structures. The energy levels and associated canonical MOs are determined as eigenspectrum of the one-electron effective Hamiltonian or the so-called Fock operator that includes the mean field interaction potential.

We have reported the development of a mean-field (or one-particle) theory to represent electron correlation at the level of the second-order Møller-Plesset perturbation (MP2) theory.[2] Orbitals and associated energy levels are given as eigenfunctions and eigenvalues of the resulting one-body (or Fock-like) MP2 Hamiltonian, respectively. They are optimized in the presence of MP2-level correlation with the self-consistent field procedure and used to update the MP1 amplitudes including their denominators. Numerical performance is illustrated in molecular applications for computing reaction energies, applying Koopmans' theorem, and examining the effects of dynamic correlation on energy levels of metal complexes.

3. Multireference Configuration Interaction Theory Using Cumulant Reconstruction with Internal Contraction of Density Matrix Renormalization Group Wave Function

We report development of the multireference configuration interaction (MRCI) method that can use active space scalable to much larger size references than has previously been pos-
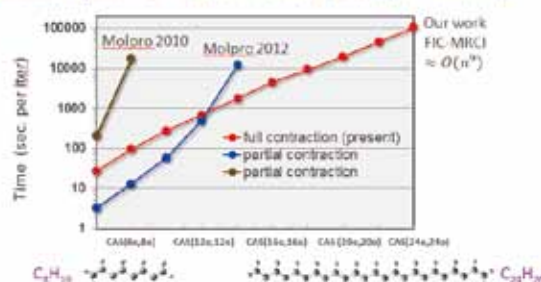

Figure 2. Calculation times (in seconds) of a single iteration including the construction of a σ vector in FIC-cu(4)-, CW-, WK-MRCI calculations for polyene molecules from C_6H_8 to $C_{24}H_{26}$ with the CAS(ne,no) reference.

sible[3] (**Figure 1**). The recent development of the density matrix renormalization group (DMRG) method in multi-reference quantum chemistry offers the ability to describe static correlation in a large active space. The present MRCI method provides a critical correction to the DMRG reference by including high-level dynamic correlation through the CI treatment. When the DMRG and MRCI theories are combined (DMRG-MRCI), the full internal contraction of the reference in the MRCI ansatz, including contraction of semi-internal states, plays a central role. However, it is thought to involve formidable complexity because of the presence of the five-particle rank reduced-density matrix (RDM) in the Hamiltonian matrix elements. To address this complexity, we express the Hamiltonian matrix using commutators, which allows the five-particle rank RDM to be canceled out without any approximation. Then we introduce an approximation to the four-particle rank RDM by using a cumulant reconstruction from lower-particle rank RDMs. A computer-aided approach is employed to derive the exceedingly complex equations of the MRCI in tensor-contracted form and to implement them into an efficient parallel computer code. This approach extends to the size-consistency-corrected variants of MRCI, such as the MRCI+Q, MR-ACPF, and MR-AQCC methods. We demonstrate the capability of the DMRG-MRCI method in several benchmark applications, including the evaluation of single-triplet gap of free-base porphyrin using 24 active orbitals.

References
1) Y. Kurashige, G. K.-L. Chan and T. Yanai, *Nat. Chem.* **5**, 660–666 (2013).
2) T. N. Lan and T. Yanai, *J. Chem. Phys.* **138**, 224108 (12 pages) (2013).
3) M. Saitow, Y. Kurashige and T. Yanai, *J. Chem. Phys.* **139**, 044118 (15 pages) (2013).