8. Computational Molecular Science Research Team

8.1. Team members

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8.2. Research Activities

Developing a Molecular Theory and Software for Predicting Reactions and Properties of Molecules

1. Employing original theory-based calculations to develop new materials and drugs

An atomic- and molecular-level understanding of drug actions and the mechanisms of a variety of chemical reactions will provide insight for developing new drugs and materials. Although a number of diverse experimental methods have been developed, it still remains difficult to investigate the state of complex molecules and to follow chemical reactions in detail. Therefore, a theoretical molecular science that can predict the properties and functions of matter at the atomic and molecular levels by means of molecular theoretical calculations is keenly awaited as a replacement for experiment. Theoretical molecular science has recently made great strides due to progress in molecular theory and computer development. However, it is still unsatisfactory for practical applications. Consequently, our main goal is to realize an updated theoretical molecular science by developing a molecular theory and calculation methods to handle large complex molecules with high precision under a variety of conditions.

2. New software makes best possible use of the processing power of the K computer

To achieve our aim, we have so far developed several methods of calculation. Examples include a way for resolving a significant problem facing conventional methods of calculation, in which the calculation volume increases dramatically when dealing with larger molecules; a way for improving the precision of calculations in molecular simulations; and a way for high-precision calculation of the properties of molecules containing heavy atoms such as metal atoms. We have integrated these calculation methods into a software package named NTChem that we are developing, which can run on the K computer and which contains a variety of high-performance calculation methods and functions. By selecting and combining appropriate methods, researchers can

perform calculations suitable for their purpose. For example, it is possible to obtain a rough prediction of the properties of a molecule in a short period of time, or obtain a precise prediction by selecting a longer simulation. In addition, NTChem is designed for high performance on a computer with many compute nodes (high concurrency), and so it makes optimum use of the K computer's processing power.

8.3. Research Results and Achievements

8.3.1. Massively parallel second-order Møller–Plesset perturbation calculations on K computer

Second-order Møller–Plesset perturbation theory (MP2) is the simplest method to account for electron correlation at ab initio level. However, the computational costs of conventional MP2 are considerably high and its practical applications are limited. For MP2 calculations the development of efficient computational techniques is important. Last year, we developed a MPI/OpenMP hybrid parallel algorithm for the massively parallel computations of resolution-of-identity MP2 (RI-MP2) method. This algorithm works efficiently on commodity supercomputers such as Riken RICC massively parallel PC cluster system. In this year, we have developed a incore algorithm suitable for the massively parallel computations on K computer. In this algorithm, the disk storage of intermediate data was replaced with memory storage to avoid the I/O overhead of accessing local scratch areas in K computer. We have implemented this new incore and MPI/OpenMP parallel RI-MP2 algorithm into NTChem quantum chemistry software developed in our team. The new implementation has been supplied as a library software on K computer. Using the new RI-MP2 codes, MP2 calculations of large molecules having up to 300 atoms and 7000 atomic orbitals can be performed with high parallel performance and in modest times on K computer. We successfully performed the RI-MP2/cc-pVTZ calculation of π-π stacked two-layer nanographene sheets ($C_{96}H_{24}$)$_2$ (6432 atomic orbitals) on K computer. The calculation was finished in 33 minutes using 2048 node and 16384 CPU cores of K computer. Using the new RI-MP2 codes, MP2 calculations of large molecules with up to 500 atoms can be performed in modest times on K computer. We have been developing the parallel RI-MP2 analytical energy gradient program enable to perform the geometry optimization calculations of molecules with about 500 atoms and ab initio molecular dynamic simulations of molecules with about 100 atoms on K computer.

8.3.2. Development of two-component relativistic coupled-cluster programs

Consideration of relativity in molecular quantum-chemical calculations is one of the most important factors for heavy-element systems. In the last financial year we developed general-order spin-free and two-component relativistic spin–orbit coupled-cluster (SOCC) programs for ground-

and excited-state correlation energies with the aid of an automatic code-generation technique. The developed generator program derives algebraic CC equations automatically for a given order, factorizes the terms in each equation, and generates Fortran programs for solving the equations. The development in this period includes (1) improvement of the generator such that level 3 BLAS routines are employed in tensor multiplications, (2) automatic algebraic derivation and solution of Lambda equations which are the key equations for computing coupled-cluster ground-state electronic properties, and (3) computation of ionization potentials through diagonalization of CC Jacobian. Excellent agreement was obtained between the calculated results using our programs and experiment for the ionization spectrum of an OsO_4 molecule, which is known to exhibit a well-known splitting due to spin-orbit interaction. The program was also tested for spin–orbit splittings of excited states of atoms and excitation energies of a TlH molecule, showing satisfactory agreements with the literature. The directions in the next financial year are: (1) large-scale parallelization and (2) development of analytical energy gradients for ground and excited states.

8.3.3. Development of analytical energy gradient for time-dependent density functional theory

Precise information on excited state potential energy surfaces is the most important prerequisite for a deeper understanding of photochemical reaction or the shape of absorption and luminescence spectra. The development and efficient implementation of an analytic gradient theory for reliable theoretical models incorporating electron correlation has been awaited. Time-dependent density functional theory (TDDFT) is widely used for excited-state calculations of various molecules. Including the electron correlation through the exchange–correlation functional, TDDFT is known to give highly accurate results in spite of the simplicity and the low-computational cost. In this work, we have implemented the analytical TDDFT gradient method in the NTChem programs. Our implementation is based on the compact fully variational derivation of the geometrical derivatives presented by Furche and Ahlrichs. Required higher-order functional derivatives of these exchange correlation functionals for the relaxed one-particle and two-particle density matrices have been derived and implemented into efficient computer codes with the aid of a newly-developed computerized symbolic algebra system. Various DFT functionals including the recently proposed range-separated hybrid functionals and meta–generalized gradient approximation (meta-GGA) functionals are applicable to the analytic energy gradient calculations for both excited singlet and triplet excited states of a closed shell molecule and for multiplet states of an open-shell molecule. In the next financial year, we will develop transition properties and nonadiabatic coupling constant matrix elements, which is the key quantity in the description of excited-state dynamics.

8.3.4. Development of relativistic quantum Monte Carlo method

We have developed a relativistic quantum Monte Carlo (QMC) method for the accurate evaluation of the electronic state of molecular systems including both electron correlations and relativistic effects. The developed method has been implemented in a program code for a massively parallel environment. The QMC method has advantage over post Hartree–Fock methods in memory requirement, scaling of computational cost, and parallelization. This is because the MC integration can be easily parallelized and has less limitation on the integrand and a compact form of wave function is available in the QMC calculation. To extend the relativistic variational Monte Carlo method, the extension to more precise diffusion Monte Carlo (DMC) method and the inclusion of spin-orbit interaction were investigated. We have developed a relativistic DMC method based on the spin-free formalism of the zeroth order regular approximation (ZORA) Hamiltonian. The Green's function is derived from the ZORA Hamiltonian and approximated in the short-time expression in the developed method. The developed ZORA-DMC method can simultaneously evaluate both electron correlations and scalar relativistic effects and its computational cost is comparable to the nonrelativistic DMC method. This research has been accepted as the article in the Journal of Chemical Physics. The spin-orbit interaction has important effects on several molecular properties e.g. spectra of transition metal systems. Following the nonrelativistic two-component extension by Ambrosetti et al., we have developed the two-component ZORA method. The developed method is implemented in the QMC program for the use in connection with spin–orbit self-consistent field (SCF) program of the NTChem program package. In order to reduce high computational cost of the QMC, a hierarchic sparse algebra library for matrices with moderate sparseness is under development. The tuning of the serial code and the development of its parallel version is now going on.

8.3.5. Development of all-electron two-component relativistic crystal orbital theory

Relativistic effects such as spin-orbit effects often take very important roles for structural and thermochemical properties of nano-materials containing heavy elements. The robust theories and methodologies have been desired for the elucidation and reliable prediction of relativistic effects in nano-materials from theoretical and computational approach. We have developed a all-electron two-component relativistic theory for periodic systems in the framework of crystal orbital theory to treat the relativistic effects in nano-materials. The theory is based on the third-order Douglas–Kroll approximation including the spin–orbit effects and the crystal orbital theory employing the periodic boundary conditions and the localized basis functions. The use of localized basis functions correctly reproduces the electronic state of atomic inner shells where the relativistic effects are significant. In our theory, Gaussian basis functions are employed for localized basis functions. The use of Gaussian basis functions makes the calculations of molecular integral easy. We also developed a spin–orbit

self-consistent field scheme employing localized Gaussian basis functions. With this method, the all-electron calculations including the scalar and spin–orbit relativistic effects can be performed for heavy elements in periodic systems with the reasonable computational costs and chemical accuracies.

8.3.6. Development of RI-PBC method for first-principles-based material simulation

There are many chemically and physically unclear phenomena in the solid-state catalysts, photovoltaic cell, solar battery, and battery reaction, where molecules intricately and varyingly interact with metal and semi-conductor surfaces. Many of surface phenomena are difficult to directly observe by experimental methods, but their deep understandings are strongly demanded to develop highly-functionalized materials and chemical systems, and therefore the powerful assistances of simulation technologies are expected. However, the periodic boundary conditions are theoretically required to consider surface systems, and its theoretical and computational treatments are under developing. In addition, calculations with the periodic boundary conditions require for much more CPU-costs compared with isolated molecular systems. So, we have been developing the RI-PBC method to reduce the calculation costs for material and surface simulations. In the RI-PBC method, the electron densities are described by auxiliary basis functions, similar to the ordinary theory for isolated molecules, but we needed additional considerations on suitable cutoff criteria and the neutrality of the unit cell. In the following fiscal year, we will brush up the RI-PBC method, and apply it for interesting surface systems.

8.3.7. HPC usability for quantum-chemistry program

First-principles quantum chemistry methods are expected to apply for various scientific and engineering fields over pure chemical areas. In order to respond to such expectations, the usability for quantum-chemistry program is required for, but it is gradually becoming difficult to develop the hilly parallelized programs with complex quantum-chemistry theories. Therefore, we study to embed a interpreter computer language into our quantum chemistry program, because interpreter languages usually have a rich description capability compared with compiler computer language such as C/C++ and Fortran. In this study, we examined the Perl, Tcl, Ruby, and Python interpreter language, and concluded that Python can be easily embedded into our quantum chemistry program without sacrificing the computational speed. Actually, we implemented the DIIS-SCF loop by Python, and the program with embedded Python can execute first-principles quantum chemistry calculations in the same computational time, compared with the pure C++ and Fortran program. We also confirmed that our Python embedding technique can be applicable for "K" computer. In the next fiscal year, we will develop and sophisticate the RI-PBC method by using this embedded Python technology.

8.3.8. Theoretical investigation of novel chemical reaction within supramolecular assembly

Supramolecular assembly has recently attracted attention because of its novel functions such as stabilization of reactive species, molecular recognition, and catalytic activity. The Raymond group reported that chiral supramolecular assembly [Ga4L6]-12 (Fig.) encapsulate a cationic substrate and show the high catalytic activity for the aza-Cope rearrangement of substrate. They also show that enantiopure (Δ or Λ structure) [Ga4L6]-12 promote the aza-Cope rearrangement enantioselectivity. While many experimental studies have been performed, the detailed mechanism of the catalytic activity and enantioselectivity are not clear. We investigated the catalytic activity and enantioselectivity of supramolecular assembly [Ga4L6]-12 by means of ab initio MO calculation. To clarify the origin of enantioselectivity, we compare two minimum energy pathways (MEPs) of aza-Cope rearrangement in which R and S structure are produced within an assembly. Differences in the stability of reactant structure, reaction barrier and length of MEP indicate that R structure is favorably produced within a Δ structure [Ga4L6]-12. We also examine the catalytic activity for aza-Cope rearrangement by comparing reaction pathway with and without assembly. Since the reaction barrier is almost same each other, it is indicated that the enthalpic contribution is dominant for rate acceleration.
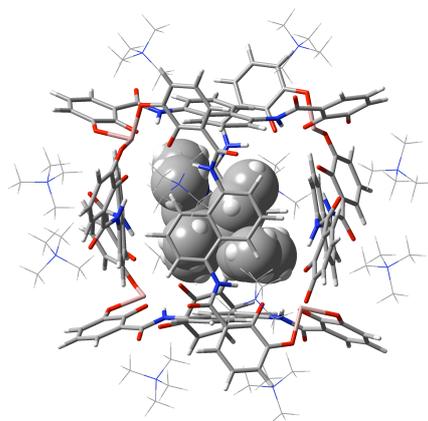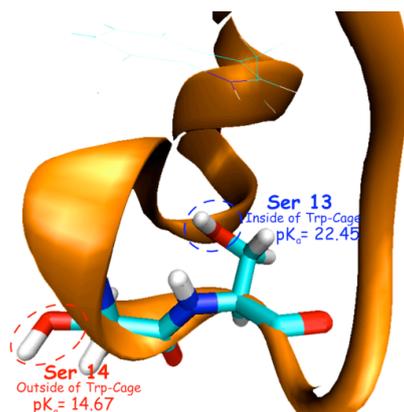

Fig. Ga4L6(L=bis(2,3-dihydroxybenzamido)naphthalen

8.3.9. New scheme to compute pKa value of amino acid

Toward the material science, the design of reaction is the most important part. Protein and its analog model complex show interesting properties and depend on the surroundings. As an example for environment dependency, each enzyme has an its optimal pH as well as optimal temperature. The pKa value is one of the criteria for the protonation of amino acid. pKa plays a key role even in chemistry, And to compute pKa is necessary for the development of the field. Nevertheless, it is surprising that no quantum chemical approach has been done for its system because of the technical difficulty such as the estimation for the energy of proton or computational costs. We here proposed a

new method to compute the pKa value on the basis of the concept for a calibration curve method. We show one of our results for pKa values of serines in Tryptophan cage (Trp-cage, 300+ atoms). From the figure below, there exists a clear difference whether OH group of serine turns outside or inside of the protein. With some assumptions, we derived the pKa values of tyrosines and serines in chignolin and a tryptophan cage. We obtained quite different pKa values of adjacent serines in the tryptophan cage; the pKa value of the OH group of Ser13 exposed to bulk water is 14.69, whereas that of Ser14 not exposed to bulk water is 22.45 because of the internal hydrogen bonds.

8.4. Schedule and Future Plan

In the next financial year, we will release the first version of the NTChem program suite on the K computer. We intend to continue adopting users' requests and to improve NTChem after its release, with the aim of making it more convenient and usable for researchers in many fields. We expect that NTChem will enable, for example, researchers to predict the structures of biological molecules as they relate to drug actions, and to elucidate the mechanisms by which nano-materials exhibit their unique functions.

8.5. Publication, Presentation and Deliverables

(1)   Journal Papers

1.   Y. Nakatsuka, T. Nakajima, "Relativistic diffusion Monte Carlo method: Zeroth-order regular approximation-diffusion Monte Carlo method in a spin-free formalism", J. Chem. Phys. 137, 154103 (2012).

2.   T. Yoshizawa, T. Nakajima, "A new computational scheme for the spin-orbit part of zero-field splitting tensor", Chem. Phys. Lett. 549, 108–112 (2012).

(2)   Conference Papers

1.   M. Katouda, T. Nakajima, S. Nagase, "Development of efficient computational techniques and codes for second-order Møller–Plesset perturbation calculation of extended systems",

Proceedings of JSST 2012, 338–343 (2012).

2. T. Nakajima et. al, Chapter 1 in "Computational chemistry for large molecules", Kagaku dojin (2012). (in Japanese)

(3) Invited Talks

1. M. Katouda, "Development of computational techniques for highly accurate quantum chemical calculations on multicore massively parallel cluster systems", Annual Meeting of Japan Society for Industrial and Applied Mathematics-Young Researchers Group, Tokyo, 26 Dec. 2012. (in Japanese)

2. T. Shimazaki "Ab-initio band structure calculation with screened Hartree-Fock (HF) exchange potential", Cambodian Malaysian Chemical Conference, Siem Reap, 19 Oct. 2012.

3. T. Shimazaki "Effects of screened Hartree-Fock (HF) exchange term on first-principle band structure calculations with periodic boundary conditions", 17th Malaysian Chemical Congress, KUALAL LUMPUR, 15 Oct. 2012.

4. T. Nakajima, "Relativistic effects on quantum chemistry (1)", CMSI summer school, Yamagata, 21 Aug. 2012. (in Japanese)

5. T. Nakajima, "Relativistic effects on quantum chemistry (2)", CMSI summer school, Yamagata, 22 Aug. 2012. (in Japanese)

6. Y. Akinaga, T. Nakajima, "Development of two-component relativistic coupled-cluster methods for molecular ground- and excited states", CJK-WTCC-2012, Beijing, 22 Jul. 2012.

7. M. Katouda, T. Nakajima, "Efficient quantum chemical calculations of macromolecules", CJK-WTCC-2012, Beijing, 20 Jul. 2012.

8. M. Katouda, "Massively parallel quantum chemical calculations with K computer", RIKEN Yokohama Institute Seminar, Yokohama, 2 Jul. 2012.

9. T. Nakajima, "Theoretical molecular science and K computer", The surface science society of Japan, Kobe, 6 Apr. 2012.

(4) Posters and presentations

1. M. Katouda, T. Nakajima, "Massively parallel second-order Møller–Plesset perturbation calculations on K computer", 3rd AICS International Symposium, Kobe, 28 Feb. 2013. (Poster)

2. Y. Nakatsuka, T. Nakajima, "Development of spin-orbit ZORA quantum Monte Carlo method for atoms and molecules", 3rd AICS International Symposium, Kobe, 28 Feb. 2013. (Poster)

3. Y. Akinaga, T. Nakajima, "Two-component relativistic general-order coupled-cluster methods for excitation energy and ionization potential", 3rd AICS International Symposium,

Kobe, 28 Feb. 2013. (Poster)

4. T. Shimazaki, T. Nakajima, "Development of first-priniciples quantum chemistry program with embedded Python interpreter", 2nd AICS International Symposium, Kobe, 28 Feb. 2012. (Poster)

5. Y. Ootani, Y. Akinaga, T. Nakajima, "Theoretical exploring of reaction pathway of aza-Cope rearrangement in supramolecular assembly", 3rd AICS International Symposium, Kobe, 28 Feb. 2013. (Poster)

6. M. Katouda, T. Nakajima, S. Nagase, "Development of efficient computational techniques and codes for second-order Møller–Plesset perturbation calculation of extended systems", JSST2012, Kobe, 27 Sep. 2012.

7. M. Kamiya, H. Sekino, T. Nakajima, "Nonlinear optical property calculations by the time-dependent density-functional method", 6th Annual Meeting of Japan Society for Molecular Science, Tokyo, Japan, 18 Sep.–21 Sep. 2012. (Poster in Japanese)

8. M. Katouda, T. Nakajima, "MPI/Open-MP hybrid parallel RI-MP2 algorithm for massively parallel calculations of large molecules", Annual Meeting of Japan Society for Molecular Science 2012, Tokyo, 21 Sep. 2012. (in Japanese)

9. Y. Ootani, Y. Akinaga, T. Nakajima, "Theoretical exploring of reaction pathway of aza-Cope rearrangement in supramolecular assembly", Annual Meeting of Japan Society for Molecular Science 2012, Tokyo, 19 Sep. 2012. (in Japanese)

10. Y. Akinaga, T. Nakajima, "Development of two-component relativistic coupled-cluster methods: application to molecular ground and excited states", 6th Annual Meeting of Japan Society for Molecular Science, Tokyo, Japan, 18 Sep. 2012.

11. Y. Nakatsuka, T. Nakajima, "Relativistic QMC approach with spin-orbit interaction", Annual Meeting of Japan Society for Molecular Science, Tokyo, 18 Sep. 2012. (in Japanese)

12. M. Katouda, T. Nakajima, "Development of two-component relativistic crystal orbital theory", 15th Annual Meeting of Theoretical Chemistry Society in Japan, Sendai, 24 May 2012. (Poster in Japanese)

(5) Patents and Deliverables
-None