5. Computational Molecular Science Research Team

5.1. Team members

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5.2. Research Activities

The primary goal of the present project is to develop our own theoretical and computational molecular theory in order to perform accurate first-principle calculations on large-size and complicated molecular systems including nano- and bio-materials. The project involves the novel development of theory, algorithm, and software with the collaborative use of the K computer. We are currently developing our own theoretical and computational approaches for molecular calculations including large-scale molecular theory, accurate molecular theory, and relativistic molecular theory. We are also developing a new software called "NTChem". The quantum chemical software forms a basis for material and biological science. However, the development of the quantum chemical software in Japan falls far short of that in Western communities. Thus, we decided to develop a comprehensive new software of ab initio quantum chemistry made in Japan from scratch. The "NTChem" program package includes our own developing theoretical approaches and is a research product of our work to develop new and better theoretical approaches. With help of the K computer, the "NTChem" suite of programs is expected to be a useful tool in various computational studies for large and complicated molecular systems. By developing our own theory and software on the K computer, we will also perform the novel computational applications for realistic molecular systems. We hope to lead the way toward a new frontier of computational molecular science.

5.3. Research Results and Achievements

5.3.1. Development of two-component relativistic coupled-cluster algorithm

Relativity is one of the indispensable ingredients in molecular electronic-structure calculations for atomic and molecular systems involving heavy-elements. The coupled-cluster (CC) method, which is one of the most successful approaches among single-reference electron correlation methods, has also been generalized into relativistic ones by several research groups. In this work, we developed

two-component relativistic CC programs considering the scalar-relativity and the spin-orbit interaction. The heart of a CC program is the multiplication of CC amplitudes to intermediates which are either bare Hamiltonian elements or Hamiltonian elements contracted to other CC amplitudes. To enable the development of the relativistic CC program with an arbitrary order excitation, we followed the automatic code-generation scheme by Kállay *et al*. Our CC code generator is capable to generate the CC program at a given order with or without spin-orbit interaction. The program imports a two-component spin-orbit SCF wavefunction calculated with the NTChem program package. In addition to the ground-state correlation energy, the program is capable to compute electronic excitation energies by diagonalizing the CC Jacobian.
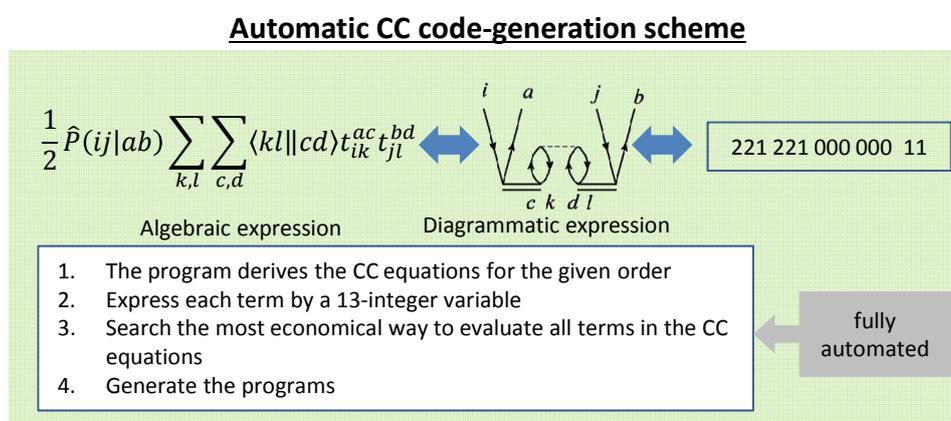
Automatic CC code-generation scheme

$$\frac{1}{2}\hat{P}(ij|ab)\sum_{k,l}\sum_{c,d}\langle kl\|cd\rangle t_{ik}^{ac}t_{jl}^{bd}$$

221 221 000 000 11

Algebraic expression   Diagrammatic expression

1. The program derives the CC equations for the given order
2. Express each term by a 13-integer variable
3. Search the most economical way to evaluate all terms in the CC equations
4. Generate the programs

fully automated

Figure. Scheme of the automatic CC code generation.

5.3.2. Development of efficient MPI/Open-MP hybrid parallel RI-MP2 algorithm

Second-order Møller–Plesset perturbation theory (MP2) is the simplest but robust electron correlation method to account for the non-covalent interactions that play important roles in the chemical phenomena of nano and biological molecules. However, the computational costs of MP2 calculations scale $O(N^5)$ with respect to the size of molecules (N), and practical applications are limited to molecules of moderate size. To make the MP2 calculations applicable to the large nano and biological molecules, the development of efficient computational techniques is desired. We have developed the parallel resolution-of-identity (RI) MP2 (RI-MP2) algorithm that is suitable for the computations of large molecule on the massively parallel supercomputers such as the K computer. In the previous parallel algorithms, the occupied orbitals are distributed to processors for the computations of two-electron integrals. However, the number of occupied orbitals is generally much smaller than that of the total molecular orbitals, so that the load balancing problems occur in the cases of the massively parallel computations. We have improved the algorithm to use the virtual orbitals for the parallel task distribution in order to make use of more large number of CPU cores with the efficient load balancing. The parallel RI-MP2 algorithm is also designed for the efficient parallel calculations by reducing the overheads of I/O and network communication. We have

implemented the new parallel RI-MP2 algorithm into the NTChem program. In this implementation, we also have performed MPI/Open-MP hybrid parallelization for the efficient usage of the memories and the network devices in the multi-core CPU architectures. We are developing the parallel RI-MP2 analytical energy gradient program enable to perform the geometry optimization calculations and ab initio molecular dynamic simulations of large molecules on the massively parallel supercomputers.
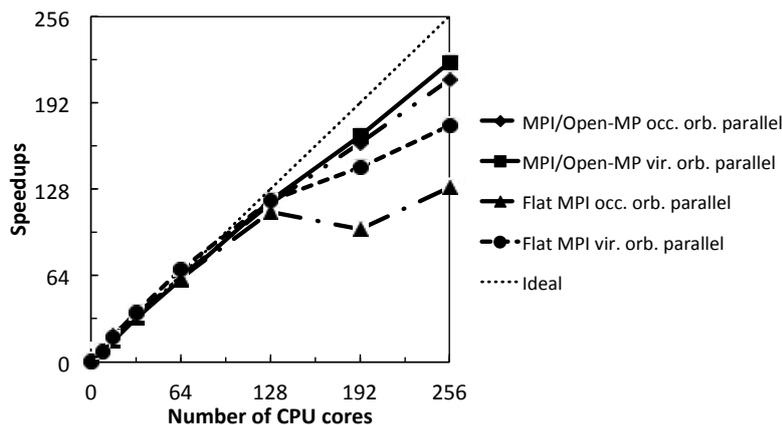

Figure. Speedups of parallel RI-MP2 calculations of taxol on the RICC massively parallel cluster

5.3.3. Development of the relativistic diffusion Monte Carlo algorithm

We have developed a relativistic extension of the quantum Monte Carlo (QMC) method which is an electron-correlation method suitable for massively parallel environment for general molecules. As the extension of the previously developed zeroth-order regular approximation variational Monte Carlo (ZORA-VMC) method, the approximate Green's function of the scalar relativistic version of the ZORA Hamiltonian and the relativistic diffusion Monte Carlo (DMC) method were derived. The ZORA-DMC method is implemented in our NTChem program package. The ZORA-DMC method can simultaneously treat the scalar relativistic effect on the total energy and the same amount of electron-correlation effects as the nonrelativistic DMC (e.g. about 96% and 91% of the estimated "exact" electron-correlation effects for Ne and Ar atom, respectively). The dissociation energy of the CuH molecule was evaluated with the ZORA-DMC calculation and the result was in the reasonable agreement with the experimental value. In this seminal year, the task parallelization has been implemented and the code achieved near 100% of the parallel efficiency with 8192 cores in the RICC system of RIKEN, Wako. Further code improvements will be performed to achieve the more flexible parallelization and the higher performance on the K computer.
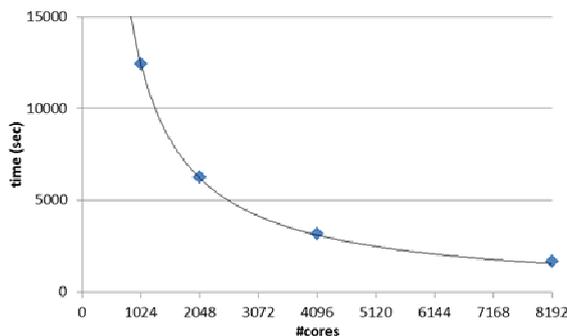
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Figure. Strong scaling of R4QMC

5.3.4. Development of time-dependent density functional theory within the Tamm-Dancoff Approximation

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. Recently, the Tamm–Dancoff approximation (TDA), which neglects the de-excitation effect in TDDFT and gives a similar formulation to the configuration interaction singles (CIS) method, has been applied to the evaluation of nonadiabatic coupling elements from the approximate TDDFT/TDA excited-state wave functions. In this work, we have implemented the TDDFT/TDA method in the NTChem programs by using the Liu-Davidson trial-vector algorithm. This implementation permits the calculations of excitation energy for both closed- and open-shell systems. The scaling of the computational cost of a TDDFT/TDA calculation per state with respect to the system size is the same as that for a Kohn-Sham calculation for the ground state. Since standard TDDFT and TDDFT/TDA exchange–correlation functionals generally underestimate excitation energies, particularly for Rydberg and charge-transfer states, we have also implemented range-separated functionals, with which charge-transfer excitation energies are generally improved. The required higher-order functional derivatives of these exchange correlation functionals have been derived and implemented into efficient computer codes with the aid of a newly-developed computerized symbolic algebra system.

5.3.5. Theoretical analysis of chemical reactions on (111) surfaces of noble metals

Adsorption of alkanethiols on noble metal surfaces has been one of the topics of interest in the field of surface science for more than 15 years. Lots of works, both experimental and theoretical, have been devoted to gain atomistic insight into the adsorption of alkanethiols and subsequent surface chemical reactions. It is well known that methanethiol (CH_3SH), the simplest alkanethiol, adsorbs molecularly to the on-top site on Au(111) surface, while methanethiolate (CH_3S) prefers the position

near the bridge site. Several computational works attempted to identify the reaction pathway of S-H dissociation of CH_3SH on Au and Cu surfaces using the NEB (Nudged Elastic Band) method. Despite that such calculations provide information which cannot be obtained experimentally, such as transition-state structures, the number of applications to surface reactions is still limited. We applied density-functional theory (DFT) to analyze the adsorption and S-H dissociation reaction of methanethiol on (111) surfaces of noble metals (Cu, Ag, and Au). Our primary purposes are: (1) identification of molecular and dissociative adsorption states, and (2) the determination of S-H reaction pathways. We used DFT with the PBE exchange-correlation functional, and the Kohn-Sham orbitals were constructed with plane-waves and pseudopotentials. The (111) surface was modeled by a four-layer slab, in which each layer contains 12 metal atoms. When optimizing adsorption structures, the atomic coordinates of the bottom layer were fixed at experimental values. We identified molecular and dissociative adsorption states of methanethiol on (111) surfaces of Cu, Ag, and Au. Moreover, we determined the reaction pathways for S-H dissociation on Cu and Au (111) surfaces using the NEB scheme. The calculated reaction pathways reveal a high energy barrier for S-H dissociation on Au(111) surface, in contrast to Cu(111) surface where the reaction is exothermic and can take place more easily than on Au(111) surface.
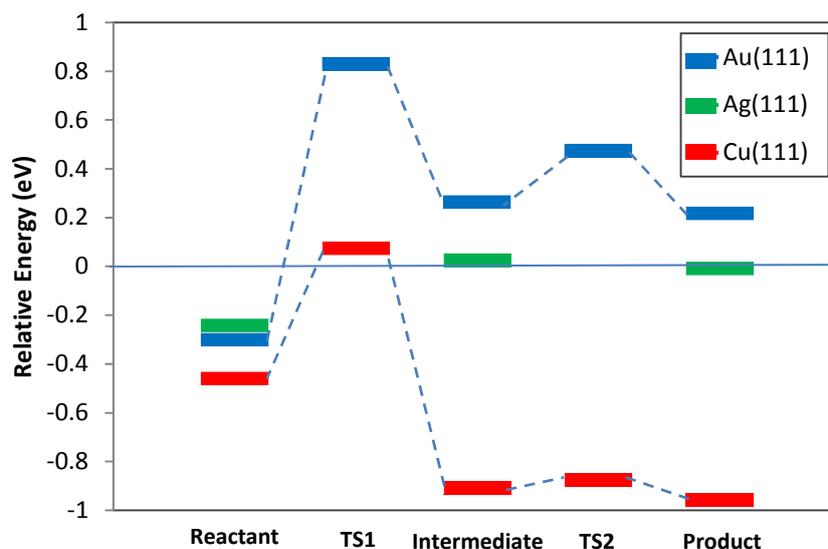

Figure. Relative energies along the methanethiol dissociation pathway on Cu, Ag, and Au (111) surfaces

5.3.6. Theoretical investigation of novel chemical reaction within supramolecular assembly

We investigated the novel chemical reaction which takes place in a supramolecule. It is reported that the aza-Cope rearrangement of allyl enammonium cation is accelerated when it is encapsulated in the cavity of M_4L_6 (M=Ga^{3+}, L=1,5-bis(2',3'-dihydroxybenzamido) naphthalene)) (Fig.). We investigated the catalytic activity of M_4L_6 by means of electronic-structure calculation. The geometry optimization was performed to locate of equilibrium structures. The reaction path for an isolated enammonium molecule was determined by means of The intrinsic reaction coordinate calculation. The Nudged Elastic Band (NEB) method was used to determine the reaction coordinate. The NEB method is a powerful tool for calculation of reaction paths of large molecular systems. By comparing the reaction path of an isolated enammonium with that of the encapsulated enammonium, we explored the catalytic activities of M_4L_6.
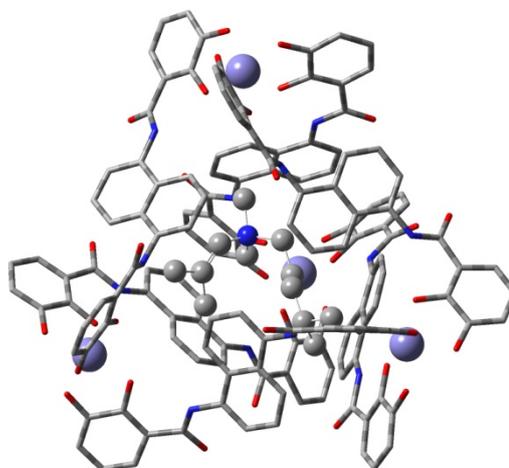

Figure. M_4L_6(M=Ga^{3+},L=bis(2,3-dihydroxybenzamido)naphthalene)

5.4. Schedule and Future Plan

In the next year, we will optimize the NTChem suite of programs on the K computer. Especially, we will highly parallelize the NTChem program on the K computer. We will also extend the functionalities of the NTChem program in order to explore the chemical reaction in the large and complicated molecular systems efficiently and accurately.

5.5. Publication, Presentation and Deliverables

(1)　Journal Papers

1. Y. Kuwahara, K. Nishizawa, T. Nakajima, T. Kamegawa, K. Mori, H. Yamashita, "Enhanced Catalytic Activity on Titanosilicate Molecular Sieves Controlled by Cation-π Interactions", J. Am. Chem. Soc. 133, 12462–12465 (2011).

2. T. Yoshizawa, T. Nakajima, "Second-order generalized unrestricted Møller–Plesset perturbation theory for the spin–orbit part of zero-field splitting tensors", Chem. Phys. Lett. 515, 296–301 (2011).

3. W. Mizukami, T. Nakajima, K. Hirao, T. Yanai, "A dual-level approach to four-component relativistic density-functional theory", Chem. Phys. Lett. 508, 177–181 (2011).

(2) Review Articles and Books

1. T. Nakajima, K. Hirao, "The Douglas–Kroll–Hess approach", Chem. Rev. 112, 385–402 (2012).

2. T. Nakajima, Y. Nakatsuka, "Relativistic quantum Monte Carlo method", in Practical Aspects of Computational Chemistry I: An Overview of the Last Two Decades and Current Trends, edited by J. Leszczynski, M. K. Shukla, H. de Rode (Springer-Verlag), 293–317 (2012).

3. Takahito Nakajima, "New Frontier for Molecular Orbital Calculation", Kagaku, 66, 24–25 (2011). (in Japanese)

(3) Invited Talks

1. Takahito Nakajima, "Relativistic effect in Chemistry", "Winter School for Quantum Chemistry", Okazaki 20 Dec. 2011. (in Japanese)

2. Takahito Nakajima, "Theoretical Molecular Science on K Computer", 82th Kinki Kagaku Kyokai Reikai, Osaka, 11 Oct. 2011. (in Japanese)

3. Takahito Nakajima, "Theoretical Molecular Science in AICS", 2nd TCCI Symposium, Kobe, 12 Aug. 2011. (in Japanese)

4. Takahito Nakajima, "Theoretical Molecular Science and K Computer", 4th Progress Quantum Chemistry Symposium, Kyoto, 30 Apr. 2011. (in Japanese)

5. Takahito Nakajima, "New Generation Molecular Science", 4th Progress Quantum Chemistry Symposium, Kyoto, 7 Apr. 2011. (in Japanese)

(4) Posters and presentations

1. Y. Akinaga and T. Nakajima, "Theoretical Study on Adsorption and Reaction of Methanethiol on Nobel Surface" 92th Annual Meeting of Chemical Society of Japan, Yokohama, 25 Mar. 2012. (in Japanese)

2. Y. Ootani, Akinaga and T. Nakajima, "Theoretical Study on Aza-Cope Reaction inside Supramolecule" 92th Annual Meeting of Chemical Society of Japan, Yokohama, 25 Mar. 2012. (in Japanese)

3. Y. Nakatsuka, T. Nakajima, "Relativistic Quantum Monte Carlo in chemistry", 2nd AICS International Symposium, Kobe, 1 Mar. 2012. (Poster)

4. M. Katouda, T. Nakajima, S. Nagase, "Development of efficient computational methods for second-order Møller–Plesset perturbation calculation of extended systems", 2nd AICS International Symposium, Kobe, 1 Mar. 2012. (Poster)

5. Y. Ootani, Y. Akinaga, T. Nakajima, "Theoretical investigation of the aza-Cope rearrangement in a supramolecular assembly", 2nd AICS International Symposium, Kobe, 1 Mar. 2012. (Poster)

6. Y. Akinaga, T. Nakajima, "Methanethiolate on noble metal surfaces: Determination of reaction paths", The 14th Asian Workshop on First-Principle Electronic Structure Calculations, Tokyo, 1 Nov. 2011. (Poster)

7. Takahito Nakajima, "EPR g tensor Calculation Based on Two-component Relativistic Molecular Theory", Annual Meeting of Molecular Science, Sapporo, 20 Sep. 2011. (in Japanese)

8. Y. Nakatsuka and T. Nakajima, "Relativistic Diffusion Monte Carlo Method", Annual Meeting of Molecular Science, Sapporo, 20 Sep. 2011. (in Japanese)

9. Y. Nakatsuka and T. Nakajima, "Relativistic Diffusion Monte Carlo Method", 14th Annual Meeting of Theoretical Chemistry, Okayama, 12-14 May 2011. (in Japanese)

10. T. Yoshizawa and T. Nakajima, "Zero-field Splitting Tensor Calculation with Two-component Relativistic Approach", 14th Annual Meeting of Theoretical Chemistry, Okayama, 12-14 May 2011. (in Japanese)