Computational Molecular Science Research Team

1. Team members

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2. Research Activities

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

2.1. 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.

2.2. 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.

3. Research Results and Achievements

3.1. Development and application of computation methods for accurate treatment of non-covalent bonding interaction of nano-scale supermolecules

Non-covalent bonding interactions often take very important roles for structural and thermochemical properties of nano-materials such as the self-assembly of supermolecules. Analysis applying robust theoretical and computational approach has been desired for the elucidation and reliable prediction of non-covalent bonding interactions in nano-scale supermolecules. Last year, we developed the MPI/OpenMP hybrid parallel algorithm and its code for the massively parallel computations of the resolution-of-identity second-order Møller–Plesset perturbation (RI-MP2) method. This algorithm works efficiently on not only commodity supercomputers such as the RIKEN RICC massively parallel PC cluster system but also the K computer. Using the new parallel RI-MP2 code, MP2 calculations of large molecules having up to 500 atoms and 10,000 atomic orbitals can be performed with high parallel performance and in modest times on K computer. In this year, we developed a code for the massively parallel computation of the double-hybrid density functional theory (DH-DFT) based on the parallel RI-MP2 code. Using the parallel RI-MP2 and DH-DFT code, we assessed the performance for π–π stacking interaction energy of two-layer nanographene sheets $(C_{24}H_{12})_2$, $(C_{54}H_{18})_2$, $(C_{96}H_{24})_2$, and $(C_{150}H_{30})_2$ at the MP2, SCS-MP2, and B2-PLYP-D3 levels with the cc-pVTZ basis set. We successfully performed the RI-SCS-MP2/cc-pVTZ calculation of $(C_{150}H_{30})_2$ (9,840 atomic orbitals) on 8,911 node and 71,288 CPU cores of K computer in 65 minutes. The results demonstrate that reliability of SCS-MP2, and B2-PLYP-D3 for the accurate calculations of the π–π stacking interaction energy: SCS-MP2 and B2-PLYP-D3 give similar results and well reproduce the experimental results while MP2 gives overestimation of results. We have also been developing the parallel RI-MP2 analytical energy gradient algorithm and its code enable to perform the geometry optimization calculations of nano-molecules with about 500 atoms on the K computer.

3.2. Application 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 2011 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 2012 includes improvement of the generator such that level 3 BLAS routines are used, automatic algebraic derivation and solution of Lambda equations, and IP-EOM (ionization potential equation-of-motion) CC equations with both spin-free and spin–orbit formalism. In this period we applied the developed method to excitation energies, potential energy curves, and ionization potentials of molecules. 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 potential energy curves are computed for ground- and excited states of TlH molecule in the level of spin–orbit EOM-CCSDT (Figure). Inclusion of full triple excitations results to the correct behavior of potential energy curves with long interatomic distances. Correct level splittings are predicted owing to inclusion of spin–orbit interaction.

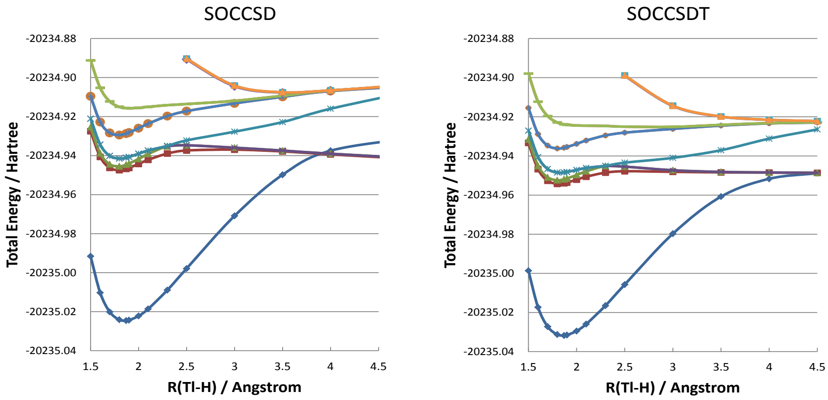


Figure: Potential energy curves of TlH at SO-CCSD and SO-CCSDT levels of theory

3.3 Development of two-component relativistic time-dependent density functional theory program with spin–orbit interaction

The inclusion of relativity is crucial for a proper description of photochemistry for systems containing heavy elements. In particular, it is known that spin–orbit coupling affects excited-state characters, relaxation dynamics, radiative and non-radiative decay pathways, as well as lifetimes and reactivity. Time-dependent density functional theory (TDDFT) has become one of the most widely used methodologies for computing excited states because of its reasonable cost and relatively high accuracy. Until now, in almost all the TDDFT calculations for heavy-element systems, only the scalar relativistic effect was taken into account while the spin-orbit coupling effect on the excitation energies was not considered. In this work, we have implemented the two-component relativistic TDDFT with spin–orbit interaction method in the NTChem programs. Our implementation is based on a noncollinear exchange–correlation potential presented by Wang et al. This formalism is suitable in relativistic TDDFT calculations with spin–orbit coupling and has the correct nonrelativistic limit and recovers the correct threefold degeneracy of triplet excitations for closed-shell systems. The matrix elements of the noncollinear exchange–correlation kernel have been derived and implemented into efficient computer codes with the aid of a newly-developed computerized symbolic algebra system. In addition, various DFT functionals including the recently proposed range-separated hybrid functionals are applicable to the calculations of excitation energy for spin–orbit coupled states.

3.4. Development of ASEP/MM for inclusion of solvent effects

The solvent effect is important in considering the relation between experimental and computational results. To investigate the effect of solvent over solute electronic structure, several methods have been proposed such as the polarizable continuum model, the reference interaction site model, and so on. We have implemented the averaged solvent electrostatic potential (ASEP) scheme in the NTChem program. The ASEP/MD scheme is a kind of the quantum mechanics/molecular mechanics (QM/MM) method, where the solvent molecule is treated in the MM calculation with the fixed solute charges and introduced in the QM calculation of solute atom in the averaged fashion. The QM and MM calculations are performed iteratively until the whole convergence. In our implementation, Tinker, which a free MM code developed in Jay Ponder group, is adopted as the MM calculation code and the iterative QM/MM cycle is built in the SCF part of the NTChem program, and users can perform ASEP/MM calculation without a cumbersome manual operation of the QM/MM iteration. The energy and gradient calculations using the ASEP/MD scheme are now available.

3.5. Development of advanced QM/MM MFEP code for supramolecules

Supramolecules (host) which contain a vacant space can contain other small molecules (guest) in the inner space, and this host–guest type complex often shows an unusual stability of a guest molecule or a characteristic reactivity. In these systems, the host molecule offers the reaction space and is supposed to interact with the included guest molecule quantum mechanically in the specific site and molecular mechanically in the remaining sites. Thus, it seems to be necessary that the host–guest reaction is investigated by the free-energy analysis. We have developed an extension of QM/MM MFEP of Hu et al. to include the guest–host QM interaction via the QM calculation of whole system and the temperature dependent interaction via the QM/MM molecular dynamics simulation. This scheme is derived from the full QM free energy expression and the temperature dependent part is approximated with QM/MM scheme. The developed extended QM/MM MFEP scheme is implemented in the NTChem program and applied to the Diels–Alder reaction in the supramolecule. In the single point calculation for the enthalpy based Diels–Alder reaction path, the reaction barrier of the free-energy is 15.5 kcal/mol whereas the reaction barrier of the enthalpy is 28.4 kcal/mol. This result shows the dynamical motion of host molecule decrease the reaction barrier of the guest molecule.

3.6. Development of the range-separation density-fitting approach for first-principles-based material quantum chemistry

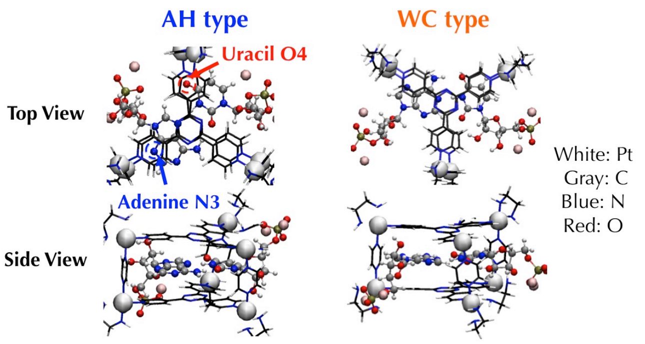
First-principles quantum chemistry methods are widely used in science and engineering, and in recent years they have been employed to investigate various materials, such as polymers, semiconductors, surface and interface systems, and bulk materials. For example, first-principles quantum chemistry methods can be used to accelerate the development of solar cells and solid catalytic systems, which are expected to contribute to solving energy and environmental problems. Thus, material quantum chemistry, which is quantum chemistry for the development of materials, is important. The electronic structure calculation under the periodic boundary conditions (PBCs) is an essential tool for material quantum chemistry. Therefore, we have developed a range-separation density-fitting method for obtaining the electronic band structure under periodic boundary conditions. The Hartree term and the nuclear attractive term are divided into long- and short-range contributions by using the error and complementary error functions, respectively. In the method, the long-range Hartree term is evaluated through a density-fitting procedure based on Gaussian auxiliary functions, where the net charge neutrality of electrons and atomic nuclei in the unit cell is ensured by Lagrange multipliers. We checked our method using the energy band structures of a two-dimensional monolayer sheet (graphene) and a three-dimensional periodic system (diamond) based on both semi-local density functional theory (DFT) functionals and the Hartree–Fock and hybrid DFT methods. From those calculations, we confirmed our method is suitable for investigating the electronic structure of materials under the PBCs. In these calculations, we also confirmed that the range-separation approach can yield good electronic structure descriptions, especially in interconnection between short- and long-range Hartree terms, because of expressive Gaussian auxiliary functions. On the other hand, the long-range contribution of the Hartree term needs much smaller CPU time than the short-range contribution, because the short-range Hartree term is estimated from heavy four-center electron-electron repulsive integrals, and thus the calculation cost to employ Gaussian auxiliary functions do not have disadvantages on the total calculation time. We only examine the basic calculations at present, and will apply the method to some important materials in the near future.

3.7. Development and implementation of a new exchange correlation functional for electronic structure calculations of periodic systems

First-principles calculations of electronic structures based on density functional theory (DFT) are today recognized as one of the most powerful tools for analyses and predictions of various properties of electronic systems. Some DFT functionals proposed so far were thus constructed to reproduce the results of numerical calculations such as quantum Monte Carlo simulations of a free-electron gas. We adopted another approach to construct a DFT functional based on the spirit of the Hedin's GW theory. The GW theory is described by the system of integral equations on the basis of the Green's function theory for a many-body electronic system, which provides electronic band structures exhibiting good agreement with the experimental ones, especially for semiconductors. We adopted a model dielectric function to construct an exchange correlation functional starting from the screened Coulomb potential. Furthermore, the Coulomb-hole interaction term was added. Such an approach has not been reported so far, to our best knowledge. Our approach may thus give insights into the relation between DFT functionals and the many-body theory based on the Green's function. We found for the various semiconductors that the calculated band gaps with the new functional are closer to the experimental values than those with the PZ81 functional are. The optimal bulk properties of the semiconductors were also examined, and we confirmed the new functional can give comparable calculation results as the PZ81 functional. These calculations corroborate the validity of our approach.

3.8. A computational approach to the selectivity of nucleobase in supramolecular cage

We investigated the mechanism of the conformation selectivity of adenine–uracil (AU) pair in supramolecular cage from the view of computational chemistry. We used a program package "NTChem" which enables us to perform a molecular calculation by a massively parallel multi-core supercomputer such as the K computer. Judging from the optimized geometry shown in the right figure, N3 of adenine and O4 of uracil mainly contribute to the broadening π orbitals and interact with pyridines in the case of anti-Hoogsteen (AH) type. When applied relativistic effect, the volume of molecular cage becomes smaller because the bond length Pt–N gets smaller in 0.1 Å and strengthens the vdW interaction between AU pair and molecular cage.



Counter ions for Pt (12x NO_3^-)are not shown.

Figure: Optimized geometries of AU pair in supramolecular cage.

According to the result of maximally interaction orbital (MIO) analyses, there exists a CH/π interaction between C5–H of uracil and a side of supramolecular cage, which stabilizes the whole structure rather than Watson–Crick type.

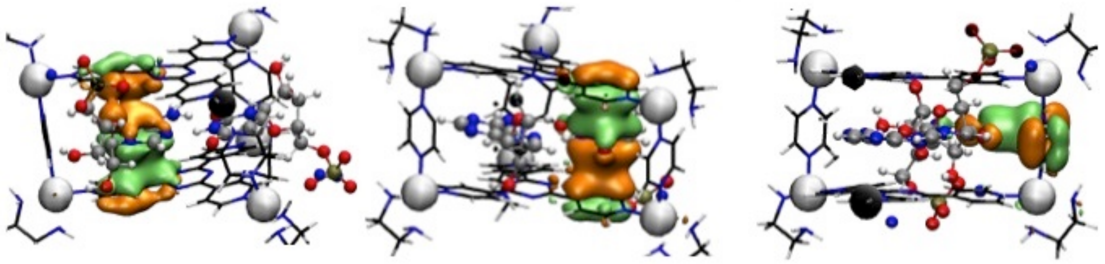


Figure: The most contributing molecular orbitals to stabilizing the AH type. (a), (b) π–π interaction between Au pair and cage. (c) CH/π interaction, seen in only AH type.

3.9. Theoretical study on a new dye-sensitizer, DX1 molecule by time-dependent density functional theory with spin–orbit interaction

Ru complexes have been demonstrated as a promising dye for a few decades. Recently, a phosphine-coordinated Ru(II) sensitizer, DX1 molecule, was reported to generate the highest value for an organic photovoltaic. The DX1 molecule has the feature that spin-forbidden singlet-to-triplet direct transitions occur because of the strong spin–orbit (SO) interaction, which indicates that the new DX1 sensitizer can avoid energy loss originating from intersystem crossing. In order to examine the spin-forbidden transitions in details, this study calculates the transition energies by two-component relativistic time-dependent density functional theory (TDDFT) with SO interaction, which was based on Tamm–Dancoff approximation (TDA) and was implemented into the quantum chemical program package, NTChem. The singlet-to-triplet transition around 1.3 eV, which is assigned to a metal-to-ligand charge-transfer type excitation, appears although it is slightly shifted to a lower energy in comparison with the experimental spectrum, probably due to lack of solvation effect. The major other peaks in the energy range from 1.5 to 3.0 eV are also reasonably reproduced with the tendency of the slight underestimation. Thus, this study confirms that two-component relativistic TDDFT/TDA calculations can reproduce spin-forbidden singlet-to-triplet transitions with reasonable accuracy. Also, the lowest peak observed for the absorption spectra of DX1 molecule is assigned to the singlet-to-triplet direct spin-forbidden transition.

4. Schedule and Future Plan

In the next financial year, we will improve the parallel efficiency of the NTChem2013 suit of program which was released on the K computer in this fiscal year. In addition, we will make

NTChem more user-friendly. We intend to continue adopting users' requests 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.

5. Publication, Presentation and Deliverables

(1) Journal Papers

[1] T. Nakajima, "Douglas–Kroll method", *Journal of Computer Chemistry, Japan*, **13**, 50–70 (2014). (in Japanese)

[2] K. Uehara, T. Miyachi, T. Nakajima, N. Mizuno, "Effect of Heteroatoms on Electronic States of Divanadium-Substituted γ-Keggin-type Polyoxometalates", *Inorg. Chem.*, in press.

[3] T. Shimazaki, T. Kosugi, T. Nakajima, *J. Phys. Soc. Jpn.*, in press.

[4] R. Sakanoi, T. Shimazaki, J. Xu, Y. Higuchi, N. Ozawa, K. Sato, T. Hashida, M. Kubo, "Different Behavior of Young's Modulus and Fracture Strength of CeO_2: Density Functional Calculation", *J. Chem. Phys.*, in press.

[5] T. Kosugi, "Repeated Extraction of Work via Measurements on Nonequilibrium Two Particles Interacting in a Harmonic Trap", *J. Phys. Soc. Jpn.* **83**, 054001 (2014).

[6] T. Kosugi, T. Miyake, S. Ishibashi, "Second-order Perturbation Formula for Magnetocrystalline Anisotropy using Orbital Angular Momentum Matrix", *J. Phys. Soc. Jpn.* **83**, 044707 (2014).

[7] S. Akamaru, T. Shimazaki, M. Kubo, T. Abe, "Density functional theory analysis of methanation reaction of CO_2 on Ru nanoparticle supported on TiO_2 (101)", *Applied Catalysis A*, **470**, 405 (2014).

[8] M. Katouda, T. Nakajima, "MPI/OpenMP hybrid parallel algorithm of resolution of identity second-order Møller–Plesset perturbation calculation for massively parallel multicore supercomputers", *J. Chem. Theory Comput.* **9**, 5373–5380 (2013).

[9] T. Kosugi, "Perpetual extraction of work from a nonequilibrium dynamical system under Markovian feedback control", *Phys. Rev.* E **88**, 032144 (2013).

(2) Invited Talks

[10] T. Nakajima, "NTChem for photosynthesis", Symposium for photosynthesis, Kobe, 8 Mar. 2014. (in Japanese)

[11] T. Nakajima, "NTChem", Supercomputer workshop 2014, Okazaki, 21 Jan. 2014. (in Japanese)

[12] M. Katouda, T. Nakajima, "MPI/OpenMP hybrid parallel algorithm of resolution of identity second-order Møller–Plesset perturbation calculation for K computer", 5th JCS International Symposium on Theoretical Chemistry, Nara, 4 Dec. 2013. (Poster)

[13] T. Shimazaki, T. Kosugi, T. Nakajima, “Development of first-principles calculation method under periodic boundary condition for material quantum chemistry”, 5th JCS International Symposium on Theoretical Chemistry, Nara, 4 Dec. 2013. (Poster)

[14] Y. Imamura, M. Kamiya, T. Nakajima, “Two-component Relativistic Time-dependent Density Functional Theory: Development and Applications”, 5th JCS International Symposium on Theoretical Chemistry, Nara, 4 Dec. 2013. (Poster)

[15] T. Nakajima, “NTChem for chemical reaction”, “New frontier for chemical reaction”, Kyoto, 28 Sep. 2013. (in Japanese)

[16] T. Nakajima, “NTChem and K computer”, TCCI symposium, Okazaki, 10 Sep. 2013. (in Japanese)

[17] T. Nakajima, “NTChem: A High-Performance Software Package for Molecular Electronic Structure Calculation on K Computer”, 6th Asia-Pacific Conference on Theoretical & Computational Chemistry, Gyeongju, 11 Jul. 2013.

(3) Posters and Presentations

[18] T. Matsui, T. Nakajima, “pKa Estimation for Side Chain of Amino Acid in Protein”, the 94th Annual meeting of Chemical Society of Japan, Nagoya, Japan, 27 Mar. 2014. (in Japanese)

[19] T. Nakajima, “NTChem: A High-Performance Software Package for Molecular Electronic Structure Calculation”, CMSI・SPring-8・J-PARC・KEK symposium 2014, Kashiwa, March, 2014. (Poster in Japanese)

[20] T. Matsui, T. Nakajima, “A Computational Approach to the Selectivity of Nucleic Acid in Supramolecular Cage”, The 63rd Conference of Japan Society of Coordination Chemistry, 3 Nov. 2013. (Poster in Japanese)

[21] T. Nakajima, “NTChem: A High-Performance Software Package for Molecular Electronic Structure Calculation”, 7th Annual Meeting of Japan Society for Molecular Science, Kyoto, Japan, Sep. 2013. (in Japanese)

[22] T. Matsui, T. Nakajima, “A Theoretical Study on the Redox Potential of metallothioneins”, 7th Annual Meeting of Japan Society for Molecular Science, Kyoto, Japan, 27 Sep. 2013. (Poster in Japanese)

[23] M. Kamiya, T. Nakajima, “Development of analytical energy gradient for two-component relativistic time-dependent density functional theory”, 7th Annual Meeting of Japan Society for Molecular Science, Kyoto, Japan, Sep. 2013. (Poster in Japanese)

[24] T. Shimazaki, T. Kosugi, T. Nakajima, “Development of ab-initio calculation method under periodic boundary conditions for material quantum chemistry”, Anuual Meeting of Japan Society for Molecular Science (2013), Kyoto, 24 Sep. 2013. (in Japanese)

[25] Y. Akinaga, T. Nakajima, “Development of two-component relativistic coupled-cluster methods: application to molecular ground and excited states”, 7th Annual Meeting of Japan

Society for Molecular Science, Kyoto, Japan, Sep. 2013. (Poster in Japanese)

[26] M. Katouda, T. Nakajima, “Development of MPI/OpenMP hybrid parallel algorithm of resolution of identity second-order Møller–Plesset perturbation calculations for massively parallel multicore supercomputers”, ISTCP-VIII, Budapest, Hungary, 29 Aug. 2013. (Poster)

[27] Y. Nakatsuka, T. Nakajima, “Development of Relativistic quantum Monte Carlo method: Theory and parallel program”, ISTCP-VIII, Budapest, Aug. 2013. (Poster)

[28] M. Katouda, T. Nakajima, “Analysis of π–π interaction of nanographene surfaces using MP2 method and dispersion corrected DFT”, 16th Theoretical Chemistry Symposium, Fukuoka, Japan, 16 May 2013. (Poster in Japanese)

(4) Patents and Deliverables

[29] NTChem2013, released on 29 Aug. 2013.