PIIa-01

MPI/OpenMP hybrid parallel algorithm of resolution of identity second-order Møller–Plesset perturbation calculation for K computer

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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 cost of MP2 calculations scales $O(N^5)$ 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 molecules, development of the efficient computational techniques is desired.

We have developed a new algorithm for massively parallel calculations of the electron correlation energy for large molecules with the resolution of the identity second-order Møller–Plesset perturbation technique [1, 2] based on the parallel RI-MP2 algorithm for the single-core PC clusters proposed previously [3]. In the new algorithm, a Message Passing Interface (MPI) and Open Multi-Processing (OpenMP) hybrid parallel programming model is applied to attain efficient parallel performance on massively parallel supercomputers. We have devised a scheme of the MPI task distribution using the virtual molecular orbitals to improve the load balancing in the massively parallel calculations. We have developed an in-core storage scheme of intermediate data of three-center electron repulsion integrals utilizing the distributed memory to eliminate input/output (I/O) overhead. We have implemented the new algorithm into the NTChem program suite [4] developed in our research team.

The parallel performance of the algorithm was tested on the K computer using up to 45,992 CPU cores. In fact, 26,554.3 times speedup was attained using 45,992 cores for the RI-MP2/cc-pVTZ calculation of π–π stacked two-layer nanographene sheets $(C_{96}H_{24})_2$ (6,432 atomic orbitals). We successfully performed a RI-MP2/cc-pVTZ calculation of π–π stacked two-layer nanographene sheets $(C_{150}H_{30})_2$ (9,640 atomic orbitals) on the K computer. The calculation was finished in 65 minutes using 8,991 node and 71,288 CPU cores of the K computer. Using the new MPI/OpenMP hybrid parallel RI-MP2 code in NTChem, MP2 calculations for large molecules having up to 300 atoms and 10,000 atomic orbitals can be performed with high parallel performance and in modest times on the K computer.

NTChem has been supplied to all users of K computer as a library program from August, 2013. It is expected that the MP2 calculations using NTChem on the K computer will become an effective approach for the material design and the biological application.

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PIIa-02

Massively Parallel Program for Quantum Chemistry Calculations

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I. Introduction

The size of calculated molecular systems is larger and larger, and nano-sized molecules are one of the challenging targets in quantum chemistry calculations. On the other hand, the number of available CPU cores continues to increase instead of improving CPU core performance because of the power and heat problems. The K computer at RIKEN consists of more than 600,000 cores with very fast interconnect. Therefore I am developing massively parallel algorithms and program in order to use supercomputers efficiently.

II. Algorithm

A massively parallel algorithm for Hartree-Fock calculations [1] is shown in Fig. 1. In the quadruple loop for the Fock assembly, the outermost loop is parallelized by OpenMP for intra-node distribution, and the third loop is parallelized by MPI for inter-node distribution. On the basis of the algorithm, exchange-correlation terms for DFT calculations are also parallelized by MPI and OpenMP in a similar manner.

III. Results

Benchmark DFT calculations were performed on the K computer (SPARC64 VIIIfx processer 2.0GHz, 8 cores/node). The system is $(C_{150}H_{30})_2$ with the cc-pVDZ basis set (4500 functions) and the number of the SCF cycles is 16. The speed-up is illustrated in Fig.2. The parallel efficiency is very high even on 98304 CPU cores, and the elapsed time on 98304 cores is 154 seconds. It is now practical to calculate nano-sized molecules using supercomputers.

```
!$OMP parallel do schedule(dynamic,1)
!$OMP reduction(+:Fock)
do μ=nbasis, 1, -1   <----- OpenMP
 do ν=1, μ
  μν=μ*(μ+1)/2+ν
  λstart=mod(μν+mpi_rank,nproc)+1
  do λ=λstart, μ ,nproc          <----- MPI
   do σ=1, λ
    Calculate (μν|λσ) and add them to Fock matrix
   enddo
  enddo
 enddo
enddo
call mpi_allreduce(Fock)
```

Fig. 1 MPI/OpenMP parallel algorithm.

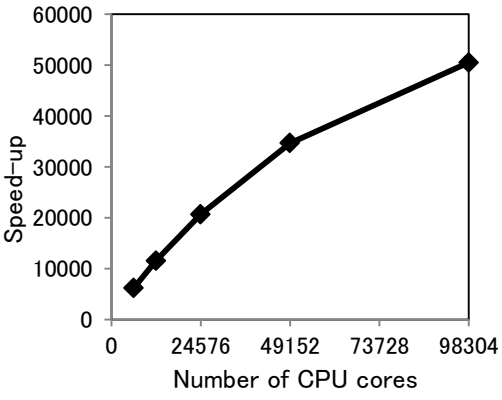

Fig. 2 Speed-up of $(C_{150}H_{30})_2$ calculation.

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PIIa-03

Model Space Quantum Monte Carlo method Hybrid Parallel Implementation and Some Applications

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We have developed the model space quantum Monte Carlo (MSQMC) method, which stochastically samples the contribution from a large secondary space to the effective Hamiltonian in the energy dependent partitioning of Löwdin [1]. The method treats quasi-degenerate electronic states on a target energy with bond dissociations and electronic excitations avoiding significant amount of the negative sign problem. The method has been implemented for efficient parallelism with the number of walkers, and the performance is demonstrated for the ground and excited states of C_2 and Cr_2 at various bond distances.

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PIIa-04

Time evolution of quantum system based on primary Rigged QED

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Quantum field theory is the most reliable theory at present. Accordingly we have developed the program package based on QED, QEDynamics [1, 2, 3]. This program package computes the time evolution of quantum fields in Heisenberg representation. Since our targets are molecules, our program treats electron, nucleus, and photon fields. Nucleus fields are included as Schrödinger fields, which is formulated in Rigged QED [4]. Electron fields are treated as two component fields. This formalism is named as Primary Rigged QED [5]. The Coulomb gauge is adopted for the quantization of photon fields [4]. Quantum fields are defined by spatial expansion functions and creation-annihilation operators. As the expansion functions of matter fields, we do not use plane waves but wave packets in a manner of Furry picture.

For the calculation of the evolution of operators, the operators at $t=t_i$ are expanded as the polynomials of operators at $t=0$ and we computes the coefficients of expansion of operators. Since the order of operators increases by interactions of many body effects, the order of the expansion polynomials increases exponentially in an instant. Hence, the expansion polynomials is truncated at some order, and some operators are evaluated by replacing the expectation values for practical computations, for details see [2, 3].

Two subjects are now tackled, thermalization and renormalization. Thermalization is closely related to the photo interactions, which are essential in QED. The thermalization is the process of the preparation of the QED Hamiltonian. By this process, the photo nature is realized, where the photons fill a system fully. The actual calculation of interactions by photon requires all the past information due to the retardation effects. Hence we compute them with some approximations explained in Ref. [3].

For the renormalization, in our case, the ordinary renormalization prescription with the asymptotic field cannot be used, since our targets are nonperturbative and nonequlibrium systems. The prescription using the conserved quantities in a system is proposed.

This work was partially supported by Grant-in-Aids for Scientific Research (25410012) and for Young Scientists (B) (24760028) from the Japan Society for the Promotion of Science and Mizuho Foundation for the Promotion of Sciences.

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PIIa-05

Development of first-principles calculation method under periodic boundary condition for material quantum chemistry

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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. So, we discuss a first-principles PBC calculation technique based on Gaussian orbital basis functions.

In this presentation, we discuss 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. 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.

Table 1 summarizes the normalized Fermi velocity of a graphene monolayer sheet obtained from various first-principles methods, based on the range-separation density-fitting approach developed. From the calculations, we can confirm that the method can reproduce the experimental result well. The details on the calculation methodology and results will be presented in the academic conference.

Table 1. Theoretical and experimental Fermi velocities of graphene monolayer sheet.

	HF	SVWN	B3LYP	Exp.
Fermi velocity [m/s]	2.51×10^6	0.86×10^6	1.18×10^6	1.093×10^6

PIIa-06

Quantum and semiclassical formulations based on overlap integrals for nonadiabatic dynamics: "Rigorous" surface hopping

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Alternative quantum and semiclassical theories for nonadiabatic dynamics are presented [1]. The nonadiabatic transitions are usually formulated by derivative couplings between adiabatic states or coupling constants between diabatic states. However, in the formulations which I present here, these terms do not appear explicitly. Instead of these coupling terms, overlap integrals between eigenstates corresponding to fast degrees of freedom are required to depict nonadiabatic propagation of quantum wave packets. For example, the overlap integrals for molecules are written as

$$\langle n;R|n';R'\rangle \quad , \tag{1}$$

where $|n;R\rangle$ is the nth electronic eigenstate for a fixed nuclear configuration R. The overlap integrals were first introduced by Schmidt and Tully for nonadiabatic expectation values under the thermal equilibrium [2], then I revealed that the overlap integrals was derived from a transformation of Schrödinger equation from the usual differential form to an integral form. Next, I applied this transformation to the semiclassical theories based on the path integral formulation since the overlap integral explicitly shows the nonlocal propagation of the probability amplitude between nuclear configurations, i.e. the R and R'. As a result, I obtained a nonadiabatic semiclassical kernel. Although this semiclassical nonadiabatic kernel is resemble to the Tully's surface hopping, there are two different features. The first features is related to the hopping. That is, the probability of hopping which conserves momentum is derived mathematically from the full quantum kernel. The second one is that this semiclassical nonadiabatic kernel includes quantum effects of the nuclei as shown in Fig 1. From these features, I call present nonadiabatic semiclassical kernel as "rigorous" surface hopping.

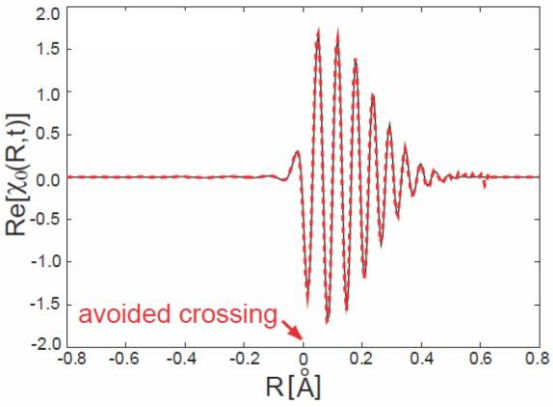

Fig. 1 Real part of a wave packet after the nonadiabtic transition. Black solid curve is numerically exact. Red broken curve is the "rigorous" surface hopping.

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PIIa-07

Automated Exploration of Novel Reaction Channels by Massively Controlled GRRM Method

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I. Automated Exploration of Reaction Channels on the Potential Energy Surface

Although it has been believed to be impossible to search the entire reaction channels for polyatomic systems [1], the anharmonic downward distortion following (ADDF) technique reveals novel aspects of reaction pathways connecting various stable structures via transition states [2-4], and the Global Reaction Mapping (GRRM) strategy becomes a powerful method for theoretical studies on chemistry [5].

II. GRRM Program

Programs for the GRRM strategy have been developed, and now GRRM11 is the most popular one [6]. GRRM11 can be operated at a parallel ADDF mode around many equilibrium structures, but it is limited within one computer (node). The author recently developed an extended version of GRRM, which makes it possible to use many nodes for the global search of reaction channels based on the ADDF.

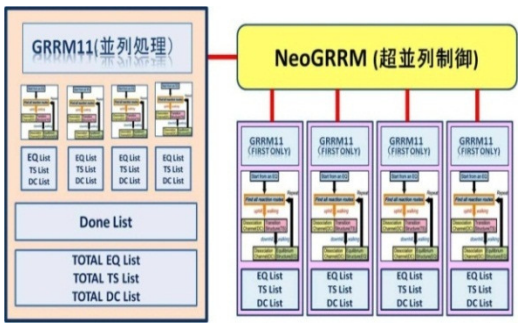

Fig. 1. Massively controlled GRRM method

III. Automated Visualization of Searched Reaction Channels

Hundreds of searched chemical structures and reaction channels require exhaustive procedures for analyses when data were treated by hands. The author developed useful tools for automated generation of visualized maps, figures, and animations, which can be seen by using a web-browser.

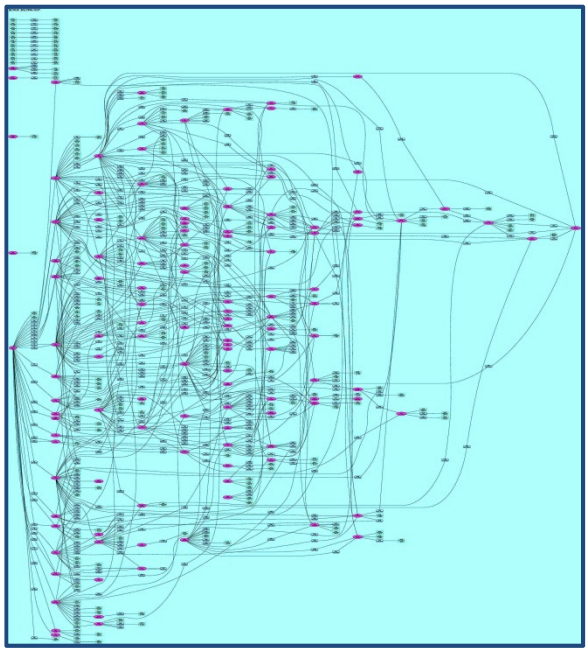

Fig. 2. Automated visualization of a global reaction route map

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[6] For details, see.
http://grrm.chem.tohoku.ac.jp/GRRM/index_e.html

PIIa-08

Direct variation of the second-order reduced density matrix: application to two-dimensional Hubbard model

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The second-order reduced density matrix method (the RDM method) has performed well in determining energies and properties of atomic and molecular systems, achieving coupled-cluster singles and doubles with perturbative triples (CCSD(T)) accuracy without using the wave-function. One question that arises is how well does the RDM method perform with the same conditions that result in CCSD(T) accuracy in the strong correlation limit. The simplest and a theoretically important model for strongly correlated electronic systems is the Hubbard model. In this paper, we establish the utility of the RDM method when employing the P, Q, G, T1 and T2' conditions in the two-dimensional Hubbard model case and we conduct a thorough study applying the 4x4 Hubbard model employing a coefficients. Within the Hubbard Hamiltonian we found that even in the intermediate setting, where U/t is between 4 and 10, the P, Q, G, T1 and T2' conditions reproduced good ground state energies.

This work is a joint work by James S. M. Anderson, Maho Nakata, Ryo Igarashi, Katsuki Fujisawa and Makoto Yamashita [1].

[1] "The second-order reduced density matrix method and the two-dimensional Hubbard model ", James S.M. Anderson, Maho Nakata, Ryo Igarashi, Katsuki Fujisawa, Makoto Yamashita, Computational and Theoretical Chemistry 1003, 22-27 (2013).

PIIa-09

Two-component Relativistic Time-dependent Density Functional Theory: Development and Applications

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I. Introduction

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. On the other hand, relativistic effects including spin–orbit (SO) interaction is not considered in a vast majority of TDDFT calculations. The recent development of organic electroluminescence diodes and photoinduced spin crossover complexes makes urgent the inclusion of SO interaction into TDDFT. Therefore, this study aims at developing two-component relativistic TDDFT with SO interaction and applying it to a dye sensitizer.

II. Computational details and application to dye sensitizer DX1

Two-component relativistic TDDFT with the spin free and dependent parts of the third and first order Douglas–Kroll Hamiltonians, respectively, was implemented into NTChem. The screened nucleus spin–orbit approximation was adopted for the spin dependent part. The basis sets used are Sapporo-DK-DZP for Ru and cc-pVDZ-DK for the other atoms. The PBE1PBE functional was adopted for TDDFT.

We calculated a phosphine-coordinated Ru(II) sensitizer, DX1 molecule, which was reported to generate the highest value for an organic photovoltaic [1]. The DX1 molecule has the feature that spin-forbidden singlet-to-triplet direct transitions occur, maybe because of the strong SO interaction. In order to examine the spin-forbidden transitions in details, this study calculates the transition energies by two-component relativistic TDDFT with SO interaction. The calculated spectrum is shown in Fig. 1. For comparison, those by the experiment and the scalar relativistic TDDFT calculation are also demonstrated. The singlet-to-triplet transition at 1.30 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 calculations can reproduce spin-forbidden singlet-to-triplet transitions with reasonable accuracy.

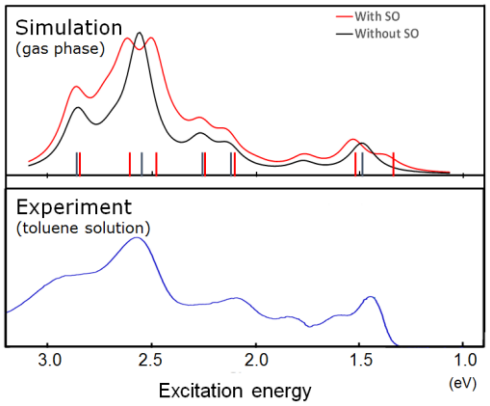

Fig. 1. Excitation spectra by experiments and by TDDFT calculations The Lorentz functions with FWHM = 0.15 eV are used for the calculated spectra.

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PIIa-10

Theoretical study on ethanolamine-water complex and ethanolamine dimer using Hamiltonian algorithm

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Chemical absorption of CO_2 using an aqueous solution of monoethanolamine [MEA, $HOCH_2CH_2NH_2$] is an important industrial method and has been studied many times both experimentally [1] and theoretically [2].

In these theoretical studies, all-trans configuration was employed, however, MEA has three single bonds in its backbone and clearly has a number of tautomers. In the present study, we try to optimize the structures of MEA, MEA + two water molecules as the model of MEA in aqueous solutions, and MEA dimer. The geometry optimization of MEA itself is easy by using the today's standard molecular orbital program package such as Gaussian09 [3], however, those of MEA + two water molecules and MEA dimer are very difficult without any additional setup. We used the Hamiltonian algorithm [4] as a setup. The Hamiltonian algorithm is useful to find unpredictable structures and we can optimize the structures of complicated molecular complex.

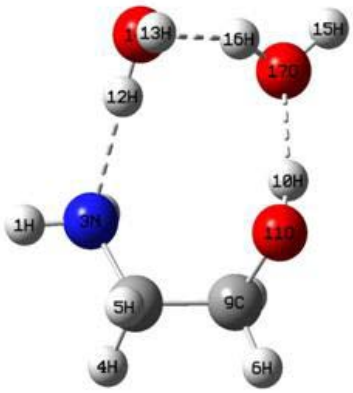

Fig. 1. The optimized structure of MEA + two H_2O.

Gaussian09 [3] and GAMESS [5] program packages are used for the molecular orbital calculations. The optimization by the Hamiltonian algorithm are performed at HF/3-21G level and the geometries are then refined by the optimization at HF/6-31++G** and MP2/6-31++G** levels.

We obtain 13 optimized structures of MEA. The most stable tautomer is a gauche structure as is considered above. Dihedral angles of the H-N-C-C-O-H backbone are calculated to be 79.3, 56.4, and -42.0 degrees, respectively, whereas those of all-trans tautomer are calculated to be 166.6, 176.4, and 172.7 degrees, respectively at MP2/6-31++G** level.

We obtained more than 30 optimized structures of MEA + two water molecules. Although we consider there are more number of configurations, we terminated the calculations within a moderate computational effort. The most stable optimized structure is shown in Figure 1, whose MEA structure is also the gauche structure. The most interesting feature of this structure is the direction of the hydrogen bond between the hydroxy group and the water molecule. The hydrogen bond is formed between the hydrogen atom of the hydroxy group and the oxygen atom of the water molecule, whereas, in the other optimized structures which are not shown here, the hydrogen bonds are formed between the hydrogen atom of water molecule and the oxygen atom of the hydroxyl group. The hydronium ion is expected to be formed easily by the proton transfer from hydroxyl group to the water molecule in the most stable structure.

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[4] H. Teramae et al., *Theor. Chem. Acc.*, **2011**, *130*, 671-678
[5] M. W. Schmidt, et al., *J Comput Chem*, **1993**, *14*, 1347-1363.

PIIa-11

A Density Functional Theory Based Protocol to Compute the Redox Potential for Transition Metal Complexes

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Toward the design of new materials at molecular level, it is helpful to understand the property of a single molecule. The redox potential is one of the most fundamental quantities of transition metal complexes (TMCs), which clarifies whether the target molecule can easily take an electron or not. The importance of measuring the redox potential of TMC is not limited to inorganic chemistry. The redox potential is one of the key information for a metal cluster to understand its catalytic property. It is also meaningful to investigate the redox potential of significant metallo-proteins, which play a crucial role for electron transfer process in biomolecules.

Recently, we have proposed a scheme to evaluate redox potential of a wide variety of transition metal complexes by adding a charge-dependent correction term for a counter ion around the charged complexes, which is based on Generalized Born theory, to the solvation energy [1]. The mean absolute error (MAE) toward experimental redox potentials of charged complexes is considerably reduced from 0.81 V (Maximum error 1.22 V) to 0.22 V (Maximum error 0.50 V). We found a remarkable exchange-correlation functional dependence on the results rather than the basis set ones. Moreover, long-range corrected (LC)-DFT well reproduces the experimental standard hydrogen electrode potentials (4.44 V).

The combination of Wachters+f (for metal) and 6-31++G(d,p) (for other atoms) with the B3LYP functional gives the least MAE 0.15 V for the test complexes. This scheme is applicable to other solvents, and heavier transition metal complexes such as $M_1(CO)_5(pycn)$ (M_1=Cr, Mo, W), $M_2(mnt)_2$ (M_2=Ni, Pd, Pt), and $M_3(bpy)_3$ (M_3=Fe, Ru, Os) with the same quality.

References

[1] T. Matsui, Y. Kitagawa, Y. Shigeta , and M. Okumura, J. Chem. Theory Comput. 9: 2974, 2013.

PIIa-12

Nano-scale modeling for automotive catalyst

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I. Modeling for automotive catalyst

Many vehicles have a close-coupled catalytic converter located near the engine's exhaust manifold. This unit heats up quickly due to its proximity to the engine, and reduces cold-engine emissions by burning off hydrocarbons from the extra-rich mixture used to start a cold engine.

In recent years, operating temperature of the catalytic converter become lower with using hybrid-system and reduction of fuel consumption system, so our research group develop and design new nano-scale materials with using some quantum chemical theory and spectroscopic study.

II. Nano-cluster and nano-scale modeling for supported materials of catalytic converter

Theoretical calculations of activation energy for NOx reduction and CO oxidation on metal cluster and ionization energy of metal cluster are performed by hybrid-DFT level. The results of NO reduction reaction are shown in Figure 1. We find volcano type plot of theoretically predicted NO reduction reaction activities of several other bimetallic cluster and the optimal point is around 6eV.

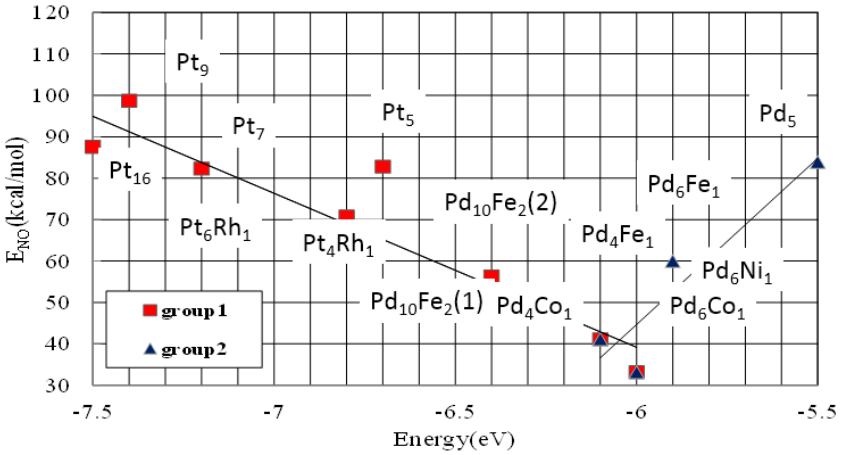

Figure 1. Volcano plot showing theoretically predicted NOx reduction reaction activities on metal cluster

PIa-13

Theoretical studies of molecular structures and magnetic properties on polynuclear metal complexes

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Polynuclear metal complexes that consist of several spin sites have attracted much attention in terms of both the basic and the applied sciences, because they are one of the promising candidates for molecular devices such as single molecular memory. Our group has studied about the relation among molecular structures, electronic structures and magnetic properties of these systems. In this presentation, we demonstrate that quantum chemical calculations can treat electronic structures, magnetic interactions of large polynuclear complexes. Here we present one example of one-dimensional Ni complexes synthesized by Peng's group in NTU i.e. $[Ni_3(dpa)_4NCS_2]$, $[Ni_5(tpda)_4X_2]$ (X=Cl, N_3, SCN etc) and $[Ni_7(teptra)_4Cl_2]$ as illustrated in Figure 1. First, their electronic structures are calculated by the unrestricted hybrid density functional theory (UHDFT) method. Because those complexes are considered to have two spins at the terminal Ni(II) ions, spin densities should appear on those Ni ions. Calculated results also support the biradical spin structure and the magnetic coupling constants (effective exchange integrals (J)) between the Ni ions can be estimated by Yamaguchi equation. In Table 1, calculated J values (J_{calc}) of the complexes are summarized. As shown in the table, calculated J values successfully reproduce the experimental ones. In addition to the magnetic properties, we also present about other properties such as conductivities.

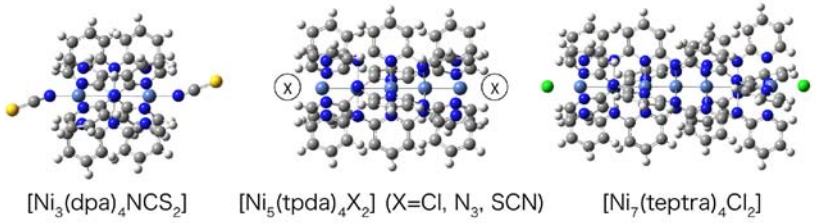

Figure 1. Calculated one-dimensional Ni complexes.

Table 1. Calculated and experimental *J* values of complexes Ni_3, Ni_5 and Ni_7 .

Complex	J_{ab} values / cm^{-1}		Complex	J_{ab} values / cm^{-1}	
	Calc.	Exptl.		Calc.	Exptl.
$[Ni_3(dpa)_4NCS_2]$	-110.8	-122	$[Ni_5(tpda)_4(N_3)_2]$	-7.7	-8.17
$[Ni_5(tpda)_4Cl_2]$	-12.6	-8.27	$[Ni_5(tpda)_4(NCS)_2]$	-9.5	-9.24
$[Ni_5(tpda)_4CN_2]$	-9.7	-6.40	$[Ni_7(teptra)_4Cl_2]$	-1.1	-3.8

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PIIa-14

Theoretical Study on Aqueous Lanthanide-Catalyzed Mukaiyama-Aldol Reaction

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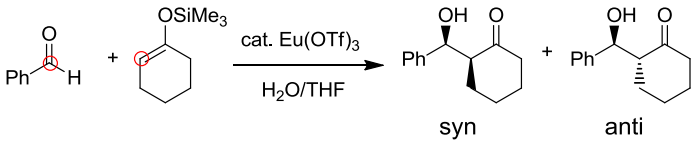
Carbon-carbon bond formations, such as Kobayashi modification of the Mukaiyama-Aldol reaction, catalyzed by lanthanide Lewis acid in aqueous solution comprise one of the most attractive types of reactions in terms of green chemistry. However, there still are unsolved questions concerning the role of water. [1] One question is why the product yield of the Mukaiyama-Aldol reaction catalyzed by $Ln(OTf)_3$ in organic solvent dramatically increased upon addition of water. Another is why the diastereoselectivity of this aqueous reaction shows *syn*-preference. To answer these two questions, the reaction pathways are explored by using the Global Reaction Route Mapping (GRRM) strategy with the B3LYP-D3 theory.



Scheme 1. Aqueous Mukaiyama-Aldol reaction catalyzed by Eu^{3+}

The most favorable reaction pathway is the stepwise reaction, starting from coordination of aldehyde to $Eu^{3+}(H_2O)_8$, followed by C-C bond formation between two substrates, proton transfer from water to aldehyde and then TMS dissociation caused by nucleophilic attack by bulk water molecules. An answer for the first question may be found by the nature of the Gibbs free energy surface of the reaction. Water can enhance the proton transfer and TMS dissociation steps, which derives the reversible C-C bond formation away from cleavage, thereby increasing the overall yield.[3]

To answer the second question about diastereoselectivity, we used the artificial force induced reaction (AFIR) method for TS sampling of the stereo-determining C-C bond formation step and found 91 *syn*- and 73 *anti*-TSs. We clarified that the entropic effect is crucial for the *syn*-diastereoselectivity in this reaction, because the hydrogen bond that restricts the conformation of the less-favored *anti*-TS is not present in the *syn*-TS.[2,3]

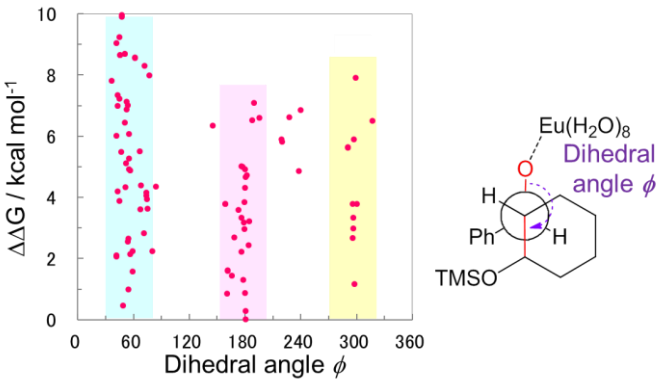


Figure 1. *syn*-TS sampling of C-C bond formation step

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PIIa-15

Predicting Free Energies of Complexation of Transition Metal-Ions with Small Ligands from the First Principles

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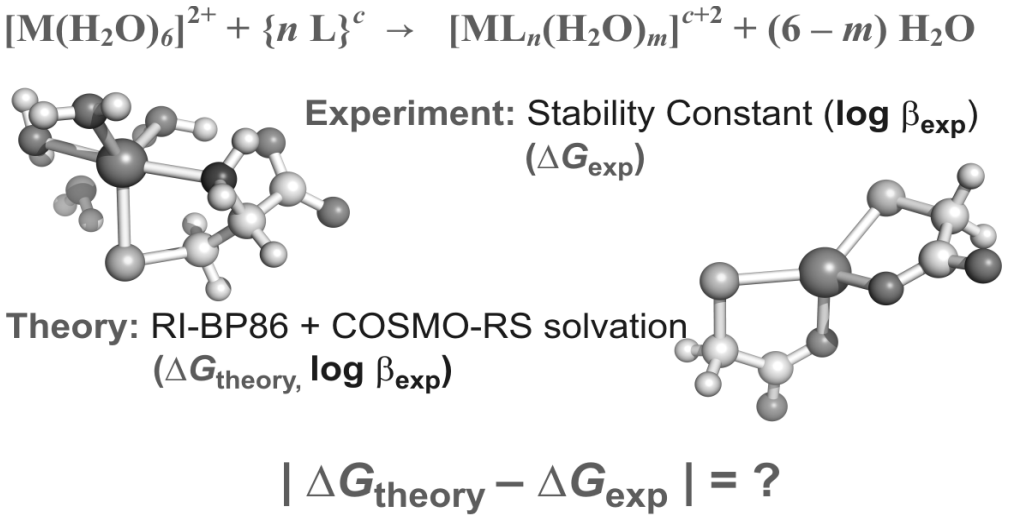
Free energy changes constitute one of the most important common grounds for computational and experimental chemists. A particularly intriguing topic that can serve as a specific example is the formation and selectivity of transition metal-ion complexes with low molecular weight ligands. These bear relevance to organic catalysis and can serve as model complexes for metalloenzymes.

At the same time, however, these systems are challenging for computational chemists due to complexity of solute-solvent interaction, especially in case of highly charged systems, which are commonly encountered in the realm of transition metal chemistry. A combination of DFT and conductor-like screening model for realistic solvation (COSMO-RS) offers a path that can unveil many insights into the topic, provided that one treads carefully.

Triumphs and issues concerning the calculation of free energies of complexation of such systems are described in the presented poster.



PIIa-16

Theoretical study of local and nonlocal molecular interactions in secondary structures

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The three-dimensional structure of a protein determines its functions and chemical properties. The second structures such as α-helices and β-sheets are important components for the protein architecture. The local and nonlocal molecular interactions, in particular hydrogen bonding, play significant roles in the formation of the secondary structures. Quantitative estimate of these interactions is required to understand the principle of the formation of the three-dimensional protein structure. In the present study, to improve the force field for accurate description of protein behavior, we have investigated the local and nonlocal molecular interactions in the α-helices and β-sheets composed of alanine residues, using quantum chemical (QC) methods (B97D/6-31+G(d)) and molecular mechanics (MM) (AMBER99-SB) . The characteristic interactions essential for forming the secondary structures are discussed quantitatively.

In the formation of antiparallel β-sheets, odd- and even-number residues contribute to the stability in a significantly different fashion, because the odd-numbered sheets form small H-bond ring structures and cause lower stability, while the even-numbered sheets form large H-bond ring structures providing higher stability. Compared to the QC calculations, the MM force field overestimates the interaction energies in the odd-numbered antiparallel β-sheets. This difference in the electrostatic repulsions causes the large discrepancy of the interaction energies, indicating the requirement of improvement of the electrostatic interaction.

Computational results using both the MM force field and quantum chemical calculations showed that almost linear relationship is found between the interaction energies and the number of peptide bonds in the formation of parallel β-sheets. This is due to the formation of almost same size of H-bond ring structures. The MM force field also overestimates the interaction energies in the parallel sheets.

The increment of the interaction energies increases together with the number of the peptide bonds in α-helices, indicating the cooperativity in the formation of α-helix due to the long-range electrostatic interactions such as dipole interactions. The MM force field stabilizes the α-helix much more than the QC method. In addition, the MM force field overestimates the interaction energies of the α-helix, compared to those of the β-sheet, implying that the improvement of the electrostatic interaction is required.

PIIa-17

Theoretical study for excited states of firefly-bioluminescence-related molecules

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Firefly luciferin, hereafter luciferin, is a substrate of bioluminescence reaction [1,2] and converted into oxyluciferin from which bioluminescence originates. To understand the mechanism of firefly bioluminescence, the spectroscopic properties of chemically stable luciferin have been studied [2–7] as an analogue of chemically unstable oxyluciferin. In particular, detailed experimental investigations for the absorption of luciferin in aqueous solutions at different pH values have been reported [3-5]. Because the luciferin molecule in solutions can take various forms of conjugate bases and conjugate acids as well as the neutral form, we have to identify which form dominates at different pH values to understand the peaks in the absorption spectra. The purpose of the present study is to investigate the absorption spectra of luciferin in aqueous solution at different pH values based on theoretically estimated pK_a values in the S_0 state. To obtain the pK_a values, we optimized the structures of luciferin and its conjugate acids and bases and performed vibrational analyses at the B3LYP/aug-cc-pVTZ level. The solvation effect in aqueous solution was taken into account by the polarizable continuum model. The concentrations of the chemical species in solutions with different pH values were estimated from their corrected pK_a values. The excitation energies and oscillator strengths were calculated by the TD-DFT method. With the theoretical absorption spectra obtained using them, the experimental spectra were unequivocally assigned. One important result is that the small peak near 400 nm at pH 1-2 is clarified to be due to the excitation of carboxylate anion with N-protonated thiazoline ring of firefly luciferin.

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PIIa-18

Correlation between experimental and theoretical electric circular dichroism spectra of biomolecules in the vacuum ultraviolet region

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Circular dichroism (CD) spectrum in the vacuum ultraviolet (VUV) region has been widely used for the precise secondary conformational analysis of protein and can be measured in some synchrotron radiation facilities in the world. CD spectra in the VUV region can be used to obtain structural information on molecules devoid of chromophores, such as saturated carbon hydrides and alcohols, as well as information on aromatic organic compounds. The establishment of an experimental and theoretical understanding of CD in the VUV region will yield non-empirical conformational analyses of many chiral substances in the future.

We succeeded in developing the CD measurement system in the VUV and extreme ultraviolet regions using the synchrotron radiation and undulator technique [1]. Recently, we have also developed the CD and linear dichroism spectra measurement system in the VUV region using a conventional VUV lamp as a light source and reduction optics, for conformational analysis of rare biomolecules such as protein and polysaccharides.

Using above systems, we have measured the VUV-CD spectra of several biomolecules, such as aliphatic amino acid films [2], sugar solutions, proteins, and polymers. Figure 1 shows the examples of VUV-CD spectra of aliphatic amino acids [2]. This result shows that VUV-CD spectra are strongly sensitive to the conformational change even of saturated alkyl groups. A reasonable prediction of these experimental spectra was obtained, even in our simple calculation based on the TD-DFT method.

In this presentation, we will report our recent results of VUV-CD spectra for biomolecules such as amino acids and sugars, and comparisons with our simple CD calculation.

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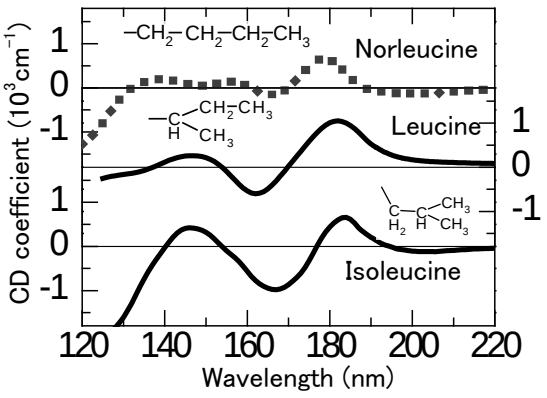

Fig. 1. VUV-CD spectra of L-norleucine, L-leucine, and L-isoleucine films in the VUV region.[2]

PIIa-19

Understanding IR spectra of perfluorinated sulfonic acid ionomer membranes

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I. Background

Perfluorinated sulfonic acid ionomers (PFSI) such as Nafion® having alkylsulfonic acid side chains have been utilized in proton exchange membrane fuel cells (PEMFC) due to their high proton conductivity and high mechanical and chemical stability. Improvement in proton conductivity at high temperature and low humidity is one of the key issues for development of low cost PEMFC and understanding structural changes of hydrated protons as well as ionomers has been highly desired. While infrared absorption spectroscopy has been the most powerful method for this purpose and a large number of quantum chemical calculations have been performed on the model systems, they have not given conclusive assignment of the observed absorption bands.

$[(CF_2CF_2)_nCFCF_2]_m$
$OCF_2CFOCF_2CF_2SO_3H$
CF_3
Molecular structure of Nafion®

II. DFT study of side chain model compounds and assignment of IR absorption bands

Recently we performed vibrational analysis of several side chain model compounds and successfully simulated their IR absorption spectra below 1500cm^{-1} [1]. Choice of PBE0 functional among popular hybrid functionals was crucial to obtain accurate vibrational frequencies of the side chain model compounds. Most of the bands in the measured IR spectra were assigned to anionic forms. While the bands of a hydrogen-bonded SO_3H dimer were confirmed in the dried samples, an undissociated monomer and its hydrated forms were absent.

III. Complex formation of hydronium ions and sulfonate anions

Completely dried PFSI membranes show a broad band at 3000cm^{-1} accompanying a small combination band of OH in-plane bending at 2400cm^{-1} in IR spectra [2]. They are not restored after hydration and subsequent vacuum drying at room temperature but shifted to 2800 and 2200cm^{-1}, respectively. Surprisingly, the spectra are identical to those of 1:1 mixture of CF_3SO_3H and water in aprotic solvents for which formation of $CF_3SO_3H^-$ H_3O^+ complex was proposed. However, this is not consistent with recent calculations that at least three water molecules are necessary for dissociation of an isolated sulfonic acid. We proposed cyclic conformers of two H_3O^+ and two sulfonates to explain acid dissociation with one water molecule and broad absorption bands in IR spectra. Results of anharmonic vibrational calculation of the complex will be presented at the symposium

This work was financially supported by the Ministry of Economy, Trade and Industry (METI) and the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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PIIa-20

Theoretical calculations of zero-field splitting parameter *D* for single molecular magnets

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I. Theoretical Background

The magnetic anisotropy is an important property of radicals. The magnetic anisotropy Hamiltonian can be expressed as

$$H = D(S_z^2 - S^2) / 3 + E(S_x^2 - S_y^2)$$

where *D* and *E* are axial and transverse zero-field splitting (ZFS) parameters. This interaction is due to spin-spin (SS) coupling and spin-orbit coupling (SOC).

For theoretical treatments of ZFS parameters, previously Pederson and co-workers have developed a method calculating the ZFS parameters (PK) with the DFT methods. In the series of our studies, we had already developed new *ab initio* MO program package ("Q" by Ryo Takeda in our group). The Pederson's treatments are also included in this program. Thus, several *ab initio* MO methods can be applied to calculating zero-field splitting parameters caused by mainly spin-orbit coupling. We examine the behavior and tendency of the method by applying it to some basic molecules such as small molecules, pure organic molecular magnets, single-molecular magnets (SMM), etc.[1-4] It shows the method has good accuracy. We suggest applicable region of the method.

In addition, Neese has also developed another calculation scheme with coupled-perturbed equation (CP). This method is involved in their program package "ORCA". Thus, we also evaluated ZFS parameters by Neese's methods.

II. Calculation

In this study we employed chiral molecular magnet $(1{\bullet}Mn(hfac)_2)_n$ (1=bis-monodentate bisaminoxyl radical, hfac=hexafluoroacetylacetonate), which was reported by Inoue and his co-workers[5]. This material possesses helical one-dimensional spin chains in its crystal. We applied PK, CP and others methods to this model and the evaluated *D* values are discuss in detailed.

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PIIa-21

Ab initio Calculation of Zero-Field Splitting Tensor in Organic Compounds

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Quantum chemical calculation of zero-field splitting (ZFS) tensor **D** of the spin Hamiltonian for excited states of molecules is a difficult task. The CASSCF theory has been frequently used for ZFS of organic molecules in excited states [1]. However, the CASSCF theory has a computationally demanding nature and its application is limited to relatively small systems. To extend applicability of theoretical calculations for ZFS of excited states, less demanding alternatives to CASSCF-based methods have been desired. Our aims in this study are development and application of a computational method for ZFS tensor **D** applicable to triplet excited states of closed-shell organic molecules with moderate costs. For this purpose, we employed the symmetry-adapted-cluster configuration-interaction (SAC-CI) theory [2]. The SAC-CI theory has been successfully applied to triplet excited states of various closed-shell molecules including considerably large systems. In organic molecules, electron spin−spin dipolar term $\mathbf{D}^{SS}$ obtained as a first order term of perturbation theory is a dominant contribution to **D**. Harriman showed that elements of theoretical $\mathbf{D}^{SS}$ tensor satisfy the equation,

$$D_{ab}^{SS} = \frac{4\beta^2}{S(2S-1)} \left\langle \Psi_n^{M_S=S} \middle| \sum_{i<j}^{\text{electrons}} \frac{\delta_{ab} r_{ij}^3 - 3(r_{ij})_a (r_{ij})_b}{r_{ij}^5} \left(2s_{iz}s_{jz} - s_{ix}s_{jx} - s_{iy}s_{jy}\right) \middle| \Psi_n^{M_S=S} \right\rangle,$$

for a reference state (M_S = S) of non-relativistic wavefunction [3]. If we insert SAC-CI wave functions into the equation, we can express $\mathbf{D}^{SS}$ tensor in terms of second-order reduced density matrix and obtain a set of equations to compute ZFS for the SAC-CI theory,

$$D_{ab}^{SS} = \frac{4\beta^2}{S(2S-1)} \sum_{pqrs}^{\text{MOs}} \Gamma_{pqrs}^{SS} \int \psi_p^*(1)\psi_q^*(2) \frac{\delta_{ab} r_{12}^3 - 3(r_{12})_a (r_{12})_b}{r_{12}^5} \psi_r(1)\psi_s(2)\, d1\, d2,$$

with

$$\Gamma_{pqrs}^{SS} = \frac{1}{2} \left\langle \Psi_L \middle| a_{p\alpha}^{\dagger\dagger\dagger\dagger\dagger\dagger} a_{q\alpha} a_{s\alpha} a_{r\alpha} - a_{p\beta} a_{q\alpha} a_{s\alpha} a_{r\beta} - a_{p\alpha} a_{q\beta} a_{s\alpha} a_{r\beta} \right.$$
$$\left. - a_{p\beta}^{\dagger\dagger\dagger\dagger\dagger\dagger} a_{q\alpha} a_{s\beta} a_{r\alpha} - a_{p\alpha} a_{q\beta} a_{s\beta} a_{r\alpha} + a_{p\beta} a_{q\beta} a_{s\beta} a_{r\beta} \left(\exp S\right) \middle| \Psi_R \right\rangle$$

where $\left(\exp S\right)\left|\Psi_R\right\rangle$ is a SAC-CI wavefunction and $\left\langle\Psi_L\right|$ is the corresponding left-side eigenvector of SAC-CI secular equation. We present explicit equations of Γ_{pqrs}^{SS} and computational results for some organic molecules.

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PIIa-22

Free energy calculations for chemical reactions in condensed phase with massively parallel QM/MM simulations

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I. Introduction

Recent computer owes its high performance to massively integrated CPUs connected with high-speed networks. This is a common feature in the modern computer architectures from laboratory size clusters to super computers. It is, hence, desirable to develop an efficient algorithm that suits massively parallel architectures for large scale electronic structure calculations. The use of real-space grid basis in representing the wave functions in KS-DFT enables the high parallel efficiency since it requires only small packet communications among neighbouring processors during the SCF iteration. In this work, we present the details of parallel implementation of our real-space grid DFT and its extension to the hybrid QM/MM simulations combined with a theory of solutions.[1] The method is applied to the computation of the free energy of hydrolysis of ATP in water solution.

II. Method and Computations

In implementing the real-space grid DFT, we utilize the norm-conserving pseudopotentials to represent the interactions between valence electrons and core ions. The Poisson equations are solved iteratively to construct the Hartree potentials, for which only the local data communications are necessitated. Atomic core regions are reinforced by the multi-grid technique to ensure the accuracy in numerical integrations near the cores. We achieved the high parallelization ratio 99.8 % for the QM part based on GGA level KS-DFT. We also examined the accuracies of our RS-DFT code by comparing the atomization energies with those obtained by Gaussian 09 with rather fine basis sets. In the QM/MM simulations, the computation of solute-solvent interactions as well as the MM energy is also parallelized with the MPI interface.

III. Results and Discussion

Our recent development enables the computation of free energy $\delta\mu$ due to the electron density fluctuations of the QM solute in response to the dynamics of the solvent water molecules.[2] The free energy $\delta\mu$ can be formulated in terms of the distribution functions for the energy associated with the solute polarization. For the hydrated whole H_4-ATP system, $\delta\mu$ was evaluated as -10.4 kcal/mol. We, thus, found that the electron density fluctuation gives non negligible effects on the energetics of the hydrolysis of ATP. The free energy contribution ($\langle E_{\mathrm{dist}} \rangle + \Delta\overline{\mu} = -25.6$ kcal/mol) due to the two-body interaction between the QM solute and MM solvent, we have total solvation free energy $\Delta\mu = -35.9$ kcal/mol.

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PIIa-23

Theoretical Simple Estimation and Accurate Evaluation of Local Aromaticity for Polycyclic Conjugated Hydrocarbons

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I. Introduction

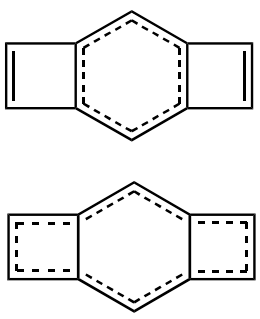
Molecular Structures and their aromaticity are very important at the fundamental information for chemistry. The structures reflect the various properties of molecules. Specifically, polycyclic conjugated molecules have some stationary point geometries (energetic local minimum), and they indicate some different physical and chemical natures. To determine the structures of these molecules theoretically, we sometimes used molecular orbital (MO) methods, density functional methods, and so on. The MO method and density functional methods determine only one structure from one intial guess geometry. So we have to provide "proper estimated initial guess geometry". In this symposium, we propose the estimation method of initial guess geometries and the electronic states systematically.

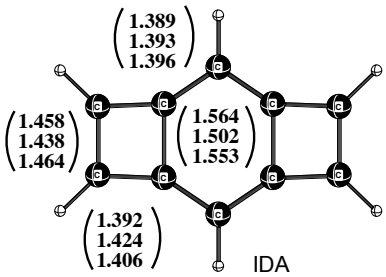
II. Methods

To estimate structures for a molecule of polycyclic conjugated hydrocarbon, we postulate two conditions. (1) Stationary point structures can be represented by one Kekulé structure or the combination of two Kekulé structures. (2) The candidate structures including element Kekulé structures of the lower stable structure are avoided. From the combination structures, we can characterize the electronic state as aromatic or anti-aromatic for the local rings of candidate structure. For the optimized geometry by the MO or density functional methods, the aromaticity of local rings was calculated by the index of deviation from aromaticity (IDA). The reliability of IDA is also indicated from the comparison of some aromatic indexes.

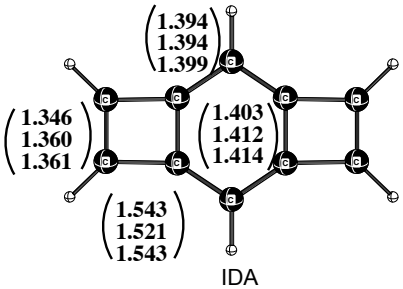
III. Results

For example, two estimation structures and computational geometries of benzo[1,2:4,5]dicyclobutene are shown below. The estimated structures correspond well to the computational geometries and aromaticity.





IDA
Four ring = 1.214
Six ring = 1.623
Whole ring = 0.349



IDA
Four ring = 3.04
Six ring = 0.363
Whole ring = 2.363

PIIa-24

Theoretical study on the electronic structures and optical response properties of one-dimensional open-shell oligomers involving five-membered rings

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In previous studies, we have theoretically found a novel structure-property relationship between the molecular second hyperpolarizability (γ the microscopic origin of third-order nonlinear optical phenomena) and the diradical character (*y* a theoretical index of degree of diradical) on the basis of the valence configuration interaction (VCI) method, i.e., open-shell singlet systems with intermediate *y* enhance γ [1]. The theoretical prediction has been evidenced from several experimental researches based on the polycyclic systems [2], but further exploration of thermally stable singlet diradical molecules in the conjugated oligomers involving heteroatoms is expected to expand the range of diradical-character-based functional molecular designing. Recently, Takahashi et al. have synthesized a new family of quinoidal oligthiophenes (QTs) where the number of thiophene rings (*n*) is ranging from one to six [3]. Interestingly, their spectroscopic and theoretical investigations revealed that the diradical nature of the system increase with the increase of *n* [3,4]. These features are considered to be closely related to their quinoidal(closed-shell)/aromatic(diradical) resonance electronic structure [4]. In this study, we investigate the relationship between the electronic structure and third-order nonlinear optical properties of QTs (**A*n*** and **B*n*** in Fig. 1) using the broken-symmetry density functional theory (BS-DFT) method along with the long-range corrected (LC-)BLYP exchange-correlation functional [5]. We here focus on the relationship among *n*, aromaticity of each five-membered ring, *y*, and γ. *n* and *y* dependences of γ are also discussed in detail based on the VCI analysis. We also compare the results with those of different family of oligothiophenes having closed-shell nature (**C*n*** and **D*n*** in Fig. 1). On the basis of the present results, we also discuss the practical design guidelines for conjugated oligomers with different diradical characters and different nonlinear optical activities.

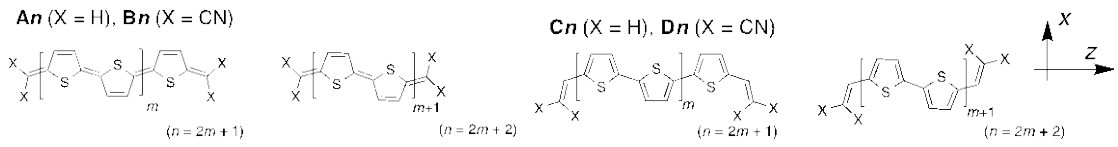

Fig. 1. Calculated molecular systems (X = H, CN)

[1] Nakano, M.; Kishi R. et al. J. Phys. Chem. A 2005, 109, 885; Phys. Rev. Lett. 2007, 99, 033001. [2] Kamada, K. et al. Angew. Chem. Int. Ed. 2007, 46, 3544; J. Am. Chem. Soc. 2013, 135, 232. [3] Takahashi, T.; Matsuoka, K.-I.; Takimiya, K.; Otsubo, T.; Aso, Y. J. Am. Chem. Soc. 2005, 127, 8928. [4] Ortiz, R. P. et al. Chem. Eur. J. 2010, 16, 470. [5] Kishi, R. et al., J. Phys. Chem. C, 2013, in press, DOI: 10.1021/jp407482h.

PIIa-25

Novel [2+1] Reaction Pathway for Disilacyclobutenes with Acetylene

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Disilacyclobutene (**1**) and benzodisilacyclobutene (**2**) thermally react with acetylenes to give disilacyclohexadienes, **3** and **4** (see Fig. 1) [1, 2]. The reaction mechanism has been considered so far that Diels-Alder reaction of the Si-Si bond cleaved intermediate (disilabutadiene) with acetylene gave the product [3]. This mechanism cannot explain the experimental results theoretically that both reactants (**1** and **2**) exhibit similar thermal reactivities, because there is a large difference between the activation energy of the ring-opening reaction of **1** and **2** (48.57 and 60.44 kcal/mol, see Fig. 2 for **2**). In addition, this mechanism cannot explain retention of stereochemistry.

Fig.1 Reactions of disilacyclobutenes with acetylene

As a result of exploring the possibility of alternative reaction pathways by extensive quantum chemical calculations, we found the entirely new reaction pathway that does not involve ring-opened intermediates and following Diels-Alder reaction [4]. As shown in Fig. 2, transition state (**TS1**) at the initial stage of the reaction, one carbon atom of acetylene directly attacks the Si-Si single bond. In **TS1**, an antibonding π* orbital of acetylene interacts with a bonding σ orbital of the Si-Si single bond similar to the [2+1] addition. Comparable activation energies for **1** and **2** (32.95 and 32.69 kcal/mol) explain that both compounds show relatively similar reactivities. It is also the only mechanism that can explain retention of stereochemistry.

Fig 2. Reaction paths for reaction between **2** and acetylene at CCSD(T)/6-311G(d,p)//ωB97X-D/6-311G(d,p)

[1] T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **1976**, 98, 7746
[2] M. Ishikawa, H. Sakamoto and T. Tabuchi, *Organometallics*, **1991**, 10, 3173-3176
[3] K. Yoshizawa, S.-Y. Kang, T. Yamabe, A. Naka and M. Ishikawa, *Organometallics* **1999**, 18, 4637-4645
[4] A. Naka, J. Ikadai, J. Sakata, M. Ishikawa, Y. Hayashi, L. Antonov, S. Kawauchi and T. Yamabe, *Organometallics*, **2013**, Online published, DOI: 10.1021/om400824p

PIIa-26

Ab Initio Molecular Orbital Studies of Aromatic Excimers and Excited States of Paracyclophanes.

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I. Introduction

Aromatic excimers have been both experimentally and theoretically investigated in the field of photophysics and photochemistry to understand their unique properties. However, the accurate ab initio studies have been limited even today. In this study, we theoretically investigate the electronic states of excimers of benzene, naphthalene, anthracene, pyrene and perylene using the multiconfiguration quasi-degenerate perturbation theory (MCQDPT) for systematical understandings [1]. The same techniques are then applied to the excited states of [2.2]-, [3.3]- and siloxane-bridged paracyclophanes (Fig. 1), which are suitable model systems for the studies of π-stacking interactions in the excited states [2].

II. Computational Details

Assuming eclipsed parallel arrangements of the aromatic dimers, the potential energy curves for the ground and excimer states were computed using MCQDPT as a function of the intermolecular distance. In the calculation of paracyclophanes, the ground and the first excited state geometries were optimized using MP2 and TD-DFT, respectively. The S_0, S_1 and S_2 states at the optimized geometries were then calculated using MCQDPT.

III. Results and Discussion

The calculated monomer absorption energies and excimer fluorescence energies are in good agreement with the experimental values, suggesting that the electronic states of these aromatic excimers are appropriately described by using MCQDPT (Table 1). The calculated inter-ring distances, *r*(R-R) of paracyclophanes in the excited states are shorter than those in the ground state, indicating excimer formation (Table 2). A drastic shortening of *r*(R-R) upon excitation is predicted for SiPCP. The S_0-S_1 transition energies well correlate with *r*(R-R), while the S_0-S_2 transition energies are almost constant. These unique behaviors can be understood on the basis of the shape of the potential energy curves of the benzene dimer.

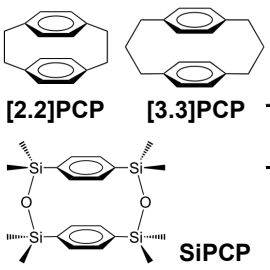

Figure 1. Structures of paracyclophanes.

Table 1: Calculated and experimental values for the fluorescence and absorption energies of the aromatic dimers (see ref. [1]).

Dimer	Flu. (eV)		Abs. (eV)	
	Calc.	Exptl.	Calc.	Exptl.
$(Benzene)_2$	3.96	3.94	4.82	4.79
$(Naphthalene)_2$	3.17	3.13	4.41	4.45
$(Anthracene)_2$	2.28	2.30	3.23	3.27
$(Pyrene)_2$	2.42	2.59	3.66	3.70
$(Perylene)_2$	1.69	1.94	2.82	2.86

Table 2: Calculated *r*(R-R) and transition enegies of [2.2]-, [3.3]- and siloxane-bridged paracyclophanes (see ref. [2]).

molecule	*r* (R-R)	transition energy	
		S_0-S_1	S_0-S_2
At the ground state optimized geometry			
[2.2]PCP	3.07	4.12	4.53
[3.3]PCP	3.24	4.34	4.77
SiPCP	3.53	4.64	4.68
At the excited state optimized geometry			
[2.2]PCP	2.95	3.70	4.44
[3.3]PCP	3.15	3.73	4.56
SiPCP	3.16	3.82	4.51

[1] Shirai, S.; Iwata, S.; Tani, T.; Inagaki, S. *J. Phys. Chem. A.* **2011**, 115, 7687.
[2] Shirai, S.; Iwata, S.; Maegawa, Y.; Tani, T.; Inagaki, S. *J. Phys. Chem. A.* **2012**, 116, 10194.

PIIa-27

Theoretical investigation of the binding of a positron to vibrational excited states of polyatomic molecules with quantum Monte Carlo method

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The positron, which is the anti-particle of the electron, is widely used in both scientific and technological areas such as physics, chemistry, material science, medicine, and their interdisciplinary areas. Positrons injected into a liquid or solid induce processes such as an ionization or electronic excitation of atoms/molecules, the formation of a metastable bound state of a positron and an electron, formation of positron-molecular complexes (positronic compound), etc., before the positron undergoes a pair-annihilation with an electron.

A positron affinity (PA), which is a binding energy of a positron to an atom or molecule, have now been experimentally measured by Surko and co-workers for many molecular species such as some hydrocarbons (alkanes, alkenes, and aromatics), alcohols, and halogenated hydrocarbons [1-3]. Their PA measurement is based on the vibrational Feshbach resonance (VFR) by incident low-energy positrons, in which the formation of a positron-molecular complex at the molecular vibrational excited states is suggested. Thus, in order to elucidate the mechanism of the positron binding to molecular vibrational excited states in detail, the theoretical analysis including the effect of the molecular vibrations is quite indispensable. In most theoretical analyses of positron-molecular complexes reported so far, however, the positron binding to molecules as well as the PA value has been analyzed only at the molecular equilibrium geometry.

In this study, thus, we developed an accurate theoretical method with combination of quantum Monte Carlo (QMC) and *ab initio* molecular orbital method in order to elucidate the effect of molecular vibrations on the positron binding, and analyzed the characteristic features of the positron binding to the vibrational excited states of some small molecules such as hydrogen cyanide (HCN), formaldehyde (CH_2O), and non-polar carbon disulfide (CS_2) molecules. In this analysis, the PA values at many molecular geometries are calculated with the configurations interaction (CI) calculation including electronic single excitation, positronic single excitation, and double excitations of single electronic - single positronic excitation configurations, and are averaged with a vibrational probability density obtained with multi-dimensional unharmonic vibrational state analysis based on vibrational QMC technique. The detail of theoretical method and obtained results will be presented on the day.

[1] Gribakin, G. F., Young, J. A., Surko, C. M., Rev. Mod. Phys. **82**, 2557 (2010).
[2] Jones, A.C.L., Danielson, J.R., Gosselin, J.J., Natisin, M.R., Surko, C.M., New J. Phys. **14**, 015006 (2012).
[3] Danielson, J.R., Jones, A.C.L., Natisin, M.R., Surko, C.M., Phys. Rev. Lett. **109**, 113201 (2012).

PIIa-28

Computational Study for Intra-molecular Tunnel Couplings: Bridge-mediated Excitation Energy Transfer / Conformational Exchange of Molecules

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I. Introduction

The tunnel coupling between degenerated states is an important parameter for the chemical kinetics and molecular spectroscopy. We have developed computational methods to investigate two different tunnel effects: the electronic coupling for the bridge-mediated excited energy transfer (EET), and the conformational exchange of the molecular geometry as the ammonia flip. In present poster, we report a difference between bridge-mediated EET mechanism of the singlet and triplet EET, and computational representation of the isotope effect in the tunnel split of ammonia flips, from these two topics, respectively.

II. Bridge-mediated excitation energy transfer

Two-state tunnel transfer is often mediated by a lot of intermediate states in its process. We have developed a method to determine such electronic intermediate states using Green's function approach to investigate a donor-bridge-acceptor system for EET. In our results (see Fig.1), the singlet EET is mediated by Förster type interactions [1,2], and the tunnel pathways for the triplet EET is based on coupled hole-electron transfers[3].

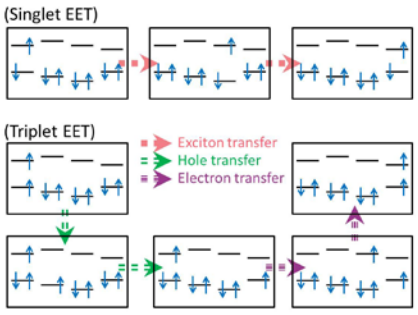

Fig 1. Tunnel pathways for singlet and triplet EET.

III. Conformational exchange of molecules

The discretized-imaginary-time path-integral instanton method [4-6] is very sensitive to the potential accuracy of molecular conformations, specially, its tunnel barrier. However, it is hard work to prepare such accurate potential functions for a lot of molecular systems. To apply the method to such various molecules, we have developed *ab initio* discretized-imaginary-time path-integral instanton program that calculates intra-molecular potential in the quantum chemical method on the fly. Using the method, we have represented the isotope effect in the tunnel split of the ammonia flip as shown in Table 1.

Table 1. Isotope effect of ammonia flips (cm^{-1}).

	Calc.	Ration to NH_3	Exp.	Ration to NH3
NH_3	0.70	1.00	0.79	1.00
ND_3	0.044	0.06	0.05	0.06
$^{15}NH_3$	0.67	0.96	0.75	0.95

[1] T. Kawatsu, J. Hasegawa, *Int. J. Quant. Chem.* **2013**, *113*, 563. [2] T. Kawatsu, J. Hasegawa, K. Matsuda, *J. Phys. Chem. C* **2012**, *116*, 13865. [3] T. Kawatsu, J. Hasegawa, *J. Phys. Chem. C* **2012**, *116*, 23252. [4] G. V. Mil'nikov, H. Nakamura, *J. Chem. Phys.* **2001**, *115* 6881. [5] J. O. Richardson, S. C. Althorpe, *J. Chem. Phys.* **2011**, *134* 054109. [6] T. Kawatsu, S. Miura, J. Phys. Conf. Ser. 2013, 454 012030. [7] To be prepared.

PIIa-29

Acute Aquatic Toxicity Considering the Reactivity of alpha, beta-Unsaturated Carbonyl Compounds

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I. Introduction

Quantitative structure–activity relationships (QSARs) are practical tools for evaluating the acute aquatic toxicities and risks of chemicals. For example, the Organization for Economic Co-operation and Development (OECD) has started the development of a QSAR Toolbox [1] "to fill gaps in (eco)toxicity data needed for assessing chemical hazards" [2]. In the OECD QSAR Toolbox, a user can evaluate the aquatic toxicities on the reactivity of chemicals [3].

α,β-Unsaturated carbonyl compounds are reactive with an electrophilic moiety that reacts with thiol groups (–SH) in proteins. That is, α,β-unsaturated carbonyl compounds are generally toxic to fish (they are sometimes more toxic than compounds that act by narcosis [4]). In this study, firstly, using schemes to present the pathway of the reactions of the compounds with a reactive SH site considering a catalytic water molecule, we performed quantum chemical calculations to determine activation energies [5]. Then, to develop a practical method for predicting the acute toxicities of a series of the compounds, we introduced linear regression equations involving Gasteiger's partial equalization of orbital electronegativity (PEOE) descriptor [6] without using 3D molecular structures to include electrostatic charge effects [7].

II. Results

The acute fish toxicities of nine of 11 α,β-unsaturated carbonyl ketones and aldehydes were evaluated to correlate with their hydrophobicities; no correlation was observed for acrolein and crotonaldehyde. The most toxic compound, acrolein, had the lowest activation energy; the activation energy of the reaction could be estimated by a reaction scheme with an explicit water molecule. However, the complexity of the reaction pathways of the compounds was reflected in the difficulty of the transition structures structure searches with the polarizable continuum model. The theoretical estimations of activation energies of α,β-unsaturated carbonyl ketones and aldehydes with more catalytic molecules or moieties including hydrogen-bond networks may complement the reaction schemes for predicting the toxicities of compounds [5].

In QSARs constructed by the PEOE and hydrophobicity descriptors for acute fish and daphnia toxicities of acrylic acids and of acrylate-like compounds, the adjusted squared correlation coefficients between measured and calculated toxicities with the lowest Akaike information criterion were high (about 0.8). Therefore the QSARs based on PEOE were practical for predicting acute toxicity, especially for α,β-unsaturated carbonyl compounds with an α-hydrogen [7].

[1] OECD QSAR project Paris. See http://www.oecd.org/env/hazard/qsar. [2] OECD Environment health and safety publications series on testing and assessment No. 58, **2006**; No. 69, **2007**, Paris. [3] Schwöbel, J.A.H.; Koleva, Y.K.; Enoch, S.J.; Bajot, F.; Hewitt, M.; Madden, J.C.; Roberts, D.W.; Schultz, T.W.; Cronin, M.T.D., *Chem. Rev.* **2011**, 111, 2562-2596 and references therein. [4] Hermens, J.L.M. *Environ. Health Perspect*. **1990**, 87, 219-225. [5] Furuhama, A.; Aoki, Y.; Shiraishi, H., SAR QSAR Environ. Res. **2012**, 23, 169-184. [6] Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, 36, 3219-3228. [7] Furuhama, A.; Aoki, Y.; Shiraishi, H., SAR QSAR Environ. Res. **2012**, 23, 731-749.

PIIa-30

Theoretical Crystal Structure Prediction with the Aid of High Performance Computing

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I. Introduction

Prediction of crystal structures is a useful computational tool for evaluating a crystal polymorphism of organic molecules in industrial fields of drug discovery and electronic device development. Furthermore, the theoretical prediction can provide immense valuable scientific knowledge on a crystal growth, optical property, and so on. Therefore, we have developed a new theoretical prediction method for organic molecular crystals with a high-speed and high-accuracy [1]. In this session, we demonstrate the predictions of crystal structures for acetylsalicylic acid (aspirin) and some organic molecules that are 14 candidate compounds (16 polymorphic forms) for the blind tests of crystal structure prediction (CSP) hosted by CCDC (Cambridge Crystallographic Data Centre). Performance tests on the parallel computing efficiencies with two supercomputers having different architectures will be also presented [2,3].

II. Methods

We performed to optimize the structures of isolated molecules of aspirin and 14 CSP-candidate molecules in the gas phase. In order to consider various molecular orientations, the optimized molecular structures were rotated around x, y, and z axes. Trial crystal structures were generated by using P21/c, P212121, P1-, P21, C2/c, Pbca, Pna21, Pnma, Pbcn. Trial crystal structures were subjected to the crystal structure optimization, and then, we listed their crystal structures based on the potential energy of the optimized crystal structures. Furthermore, we compered the calculated crystal structures with the experimental ones. In the predictions, we applied the MMFF94 potential.

III. Results and Discussion

Our crystal structure predictions of CSP-candidates are reached to 19 % in the rate of correct answer. This result is superior to the other CSP methods (15 % correct). We also examined some performance benchmark tests using two different supercomputer systems. The parallel efficiencies are shown in Fig. 1. These results will be discussed in the poster session.

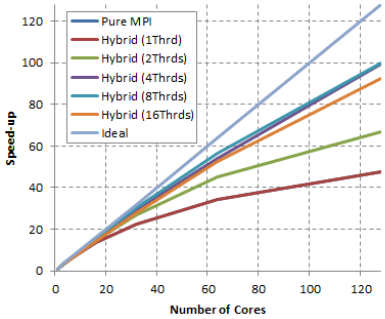

Fig. 1 Speed-up rate of crystal structure optimization using pure-MPI and hybrid MPI/OpenMP calculations

[1] H. Goto, S. Obata, N. Nakayama, K. Ohta, CONFLEX 7; Conflex: Tokyo, Japan, 2012. [2] S. Obata, H. Goto, J. Comput. Aided Chem., 2008, 9, 8-16. [3] S. Obata, H. Goto, J. Comput. Chem. Japan, 2008, 7, 151-164.

PIIa-31

Difference Density Matrix Analysis: Application to Substituent Effects and Intermolecular Interactions

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I. Introduction

The size of molecules calculated by molecular orbital (MO) theory is becoming huge with the development of computation power and algorithms. To compare between such huge molecule and another similar molecule is difficult because it is virtually impossible to use the conventional MO-analysis i.e. investigating the subtle difference between two sets of MOs for huge molecules. To overcome this situation, we have proposed the difference density matrix analysis method, which enable us to focus on the active part of electronic states (See Fig. 1). In this paper we show applications of this analysis method to the substituent effects on nitrobenzene in order to demonstrate the usefulness of this method.

II. Difference Density Matrix Method

In the difference density matrix analysis method, natural orbitals (NOs) and occupation numbers (eigenvalues) of difference density matrix (Δρ) between two molecules are used (See the equation in Fig. 1). Among non-integral occupation numbers, there are one-to-one correspondences between positive and negative values for RHF-based density matrices. For example, if there is an orbital with occupation number +0.3, then there always exists an orbital with -0.3. These pairs of orbitals can be interpreted as electron-transfers or excitation between them. The absolute values of occupation numbers indicate the numbers of transferring or excited electrons. Orbital-pairs with small occupation (close to 0) are not important and can be neglected. Therefore one can focus on analysis of orbital-pairs with large absolute values.

III. Results

To analyze the substituent effects on nitrobenzene, the natural orbitals (NOs) of Δρ=ρ(nitrobenzene) – ρ(benzene) are calculated. The dominant orbital-pairs of the NOs are shown in Fig. 2. The orbital-pair with largest occupation ±0.55 indicates an electron-transfer from the σ-orbital located in the carbon atom to the σ-orbital in the nitrogen atom, which shows the inductive effects. The orbital-pair with 2nd largest occupation ±0.37 indicates an electron-transfer from the π-orbital in the ortho and para positions to the π-orbital of nitro-group, which shows the resonance effects. Our analysis successfully detects the inductive and resonance effects of the substituent effects by investigating a few orbital-sets. It is found that our method is useful to compare the molecules.

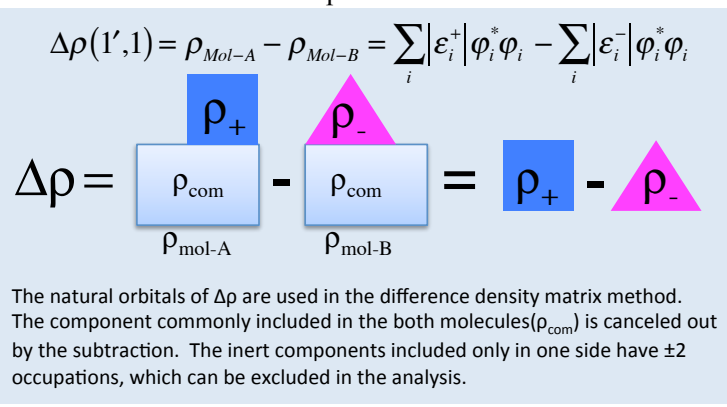

Fig. 1. Difference Density Matrix Method (extraction of active part)

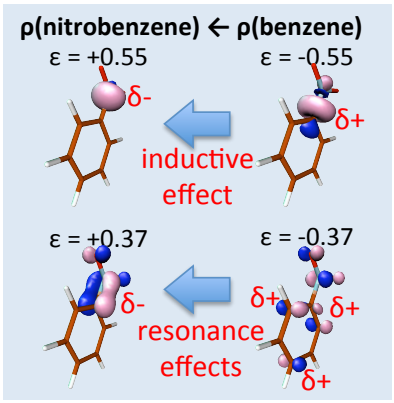

Fig. 2. Analysis of Substituent Effects. (Two dominant orbital-pairs; Inert orbitals of NO_2 with ε=+2.0 were excluded.)

PIIa-32

Quantum interference effect observed in the angular momentum polarization and the branching ratio of photofragments of simple molecules

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I. Introduction

Recent studies of molecular photodissociation enable us to investigate quite detailed information on the dissociation dynamics. Special interest has been devoted to molecules with open-shell fragments with nonzero spin and orbital angular momenta, since they exhibit nonadiabatic interactions in the angular momentum recoupling regions. Therefore, detailed studies of anisotropy parameters, product branching ratios, and orientation and alignment of angular momentum of photoproducts have been carried out. If a diatomic molecule is excited to two excited states and both are led to an identical quantum state of the photoproduct, quantum interference can be observed in various quantities. Some examples are shown in this theoretical work.

II. Theoretical methods

Spin-orbit CI method has been used to compute the transition moments, potential curves, as well as non-adiabatic coupling elements. Quantum wavepacket, semiclassical, and classical path methods have been used for dynamics calculations.

III. Results

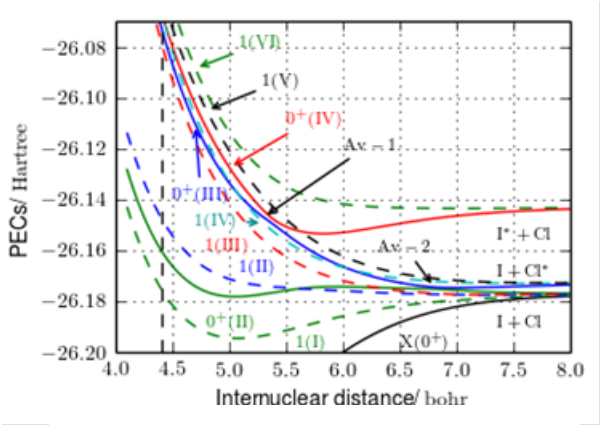

Fig. 1 Lower-lying electronic states of ICl.

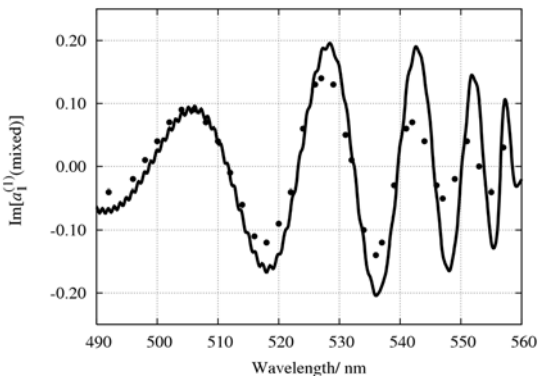

Fig.2 l-dependence of the angular momentum polarization parameter.

As Fig.1 shows, an ICl molecule can be excited simultaneously to the 1(I)($A^3\Pi_1$) and 0^+(II) ($B^3\Pi_{0+}$) states, both of which correlate to the product channel of Cl($^2P_{3/2}$). Fig.2 shows the first-rank angular momentum polarization parameter whose interference pattern is in good agreement with experiment by Alexander et al.[1,2] Fig.1 also shows that both the 0^+(III) and 0^+(IV) states are involved in the second absorption band and exhibit an avoided-crossing (Av-1) at R=5.3a_0. Our dynamics calculation shows the product branching ratios exhibit a significant interference effect almost independent of the excitation energy. The F_1 and F_2 spin-rotation levels of the product CN($^2\Sigma^+$,N) created from the photodissociation of ICN has been known to exhibit non-statistical distributions. We will explain the interference pattern based on the calculated potential energy surfaces.

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PIIa-33

DFT-MD Studies on Redox Reactions on Solid-Solution Interfaces in Battery and Solar Cell

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The Redox reactions (electron transfer) at solid-liquid interfaces play crucial roles in diverse topics in energy and environmental issues, such as Lithium ion battery (LIB), dye-sensitized solar cell (DSSC), fuel cell and photocatalysis. Although many developments have been already made in these fields, the atomistic mechanisms have been still open questions. In order to understand such processes and suggest how to increase the efficiencies theoretically, we have been working on the establishment of DFT-MD sampling methods for free energies of redox reactions as well as solid-liquid (electrolyte) interfaces in batteies, solar cells and catalysts [1-6].

In this presentation, I'll introduce our recent works on the LIB electrolytes [1] and the interfaces of DSSC [2,3]. For the former topic, we have investigted reductive decomposition and initial formation of solid electrolyte interphase (SEI) of a ypical LIB electrolyte with EC solvent and VC additives near the negative electrode, by using DFT-MD sampling and Blue-moon ensemble method for the free energy profiles[1]. Examining possible processes under 1-electron and 2-electron reductions as well as radical attack, we elucidated the VC additive effect on increase of the SEI character, which may lead to the improvement of LIB performance. Regarding the DSSC, we have investigated the adsorption state of a most efficient Ru dye on TiO_2 anatase (101) surface, as well as the equilibrium state of TiO_2/acetonitrile (AN) electrolyte interfaces [2,3]. Using statistical analysis as well as TDDFT technique, we suggested a novel picture of TiO_2/Dye/AN interface in DSSC. This will give a useful perspective for the atomistic mechanism of DSSC.

[1]K. Ushirogata, K. Sodeyama, Y. Okuno, Y. Tateyama, J. Am. Chem. Soc., 135, 11967 (2013).
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PIIa-34

Towards Accurate Calculation of Free Energies in Gas-Phase and Solution by Quantum Chemistry

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I. Introduction

Enthalpy, entropy and free energies are significantly important thermodynamic parameters, but quantum chemical method for calculate these values in solution is quite insufficient. In some cases, researches still use gas-phase equation even at liquid phase, which causes large error at free energy calculation. In this study, we propose a new method for enthalpy and entropy evaluation in solution, to give accurate free energies by quantum chemical method.

II. Methods

Here we propose two methods for entropy evaluation in solution; (A) entropy evaluation assuming separation of translational, rotational, and vibrational motions, and (B) entropy evaluation treating all solute's motion by vibration. In (A), we first determine solute-solvent interaction by image-charge method, and after that we solve the rotational eigenvalue equation numerically. This gives the rotational energy levels, and thus the partition function and entropy are calculated. In method (B), we define solute's cavity and translational and rotational modes are considered as soft vibration within that cavity.

III. Results

For test calculations we evaluated dissolution entropy and standard Gibbs energy change for water formation by our new-entropy evaluation method, and these are shown in Table 1. Entropies or Gibbs energies calculated by translation-correction only is also shown. From Table 1, our method clearly improves the entropy and Gibbs energy values. Details of our method, other applications will be presented at the JCS conference.

Table 1. Entropy and Gibbs energy computational results by old and our new entropy evaluation methods.

Dissolution entropy (J/mol/K)			
Solute (Solvent)	Old method	Our method	Experiment
CO_2 (ethanol)	45.6	85.8	80.3
HCl (CH_3Cl)	38.5	58.6	74.5
Ethane (H_2O)	47.3	90.4	111.3
Standard Gibbs energy of formation (kJ/mol)			
H_2(gas) + (1/2)O_2(gas) = H_2O(liquid)	-226.9	-236.4	-237.3

PIIa-35

Relativistic coupled cluster studies for electron's electric dipole moment arising from Charge-Parity violation

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The electric dipole moment of the electron (eEDM, or namely d_e) is an important probe of Charge Conjugation-Parity (CP) symmetry violation. The search for d_e has gone on for almost a half century, but so far it has not been observed. However, its upper limit has gradually become lower during this time. A recent molecular experiment using ThO[1] provides the best limit for d_e as lower than 0.87×10^{-28} [e cm] at 90% confidence level. This is an order of magnitude improvement over the previous best limit which came from YbF.[2] Attempts are currently under way to improve the limit for YbF, and a new result is expected in the near future. Direct measurement of the value of d_e in the molecule is not possible but the interaction energy between d_e and internal electric field $\mathbf{E}_{int}$ inside the molecule can be measured. This interaction energy is shown in eq. (1).

$$\left\langle \Psi \left| \tilde{H}_E \right| \Psi \right\rangle = d_e \left\langle \Psi \left| \sum_i^{N_e} \beta_i \boldsymbol{\sigma}_i \cdot \mathbf{E}_{int} \right| \Psi \right\rangle = d_e E_e \quad , \qquad (1)$$

where β is a Dirac matrix and σ are spin matrices. The net electric field acting on an electron inside a molecule is called the effective electric field (E_{eff}). We can obtain the value of E_{eff} only from relativistic molecular orbital calculations. It is possible to extract d_e by combining the measured value of the interaction energy with the calculated value of the effective field. Therefore accurate relativistic calculations of E_{eff} are indispensable for the search of eEDM.

In this study, we have developed a rigorous method to calculate E_{eff} in polar molecules. We have used the relativistic coupled cluster singles and doubles (RCCSD) method based on the Dirac-Coulomb Hamiltonian. We have modified and combined the UTChem and DIRAC08 codes for this purpose. We have calculated E_{eff} for YbF molecule using the Dyall's triple-zeta (TZ) or quadruple-zeta (QZ) basis in uncontracted form. We obtain the value of E_{eff} as 22.8 GV/cm in our best calculation, where we have used 49-active electrons in 656 active-spinor space. This is calculated using the QZ basis, one of the most accurate relativistic basis sets. Our best permanent dipole moment is 3.59 Debye while the experimental counterpart is 3.91 Debye. The error in PDM from the experiment is 8%. Since both the E_{eff} and PDM are enhanced by s-p mixing of orbitals, the error in E_{eff} can be of similar amount.

Reference [1]http://arxiv.org/pdf/1310.7534.pdf [2]J. J. Hudson et *al*. Nature, **473,** pp495 (2011).

PIIa-36

Theoretical Study of the Substituent and Solvent Effects on Azide-Tetrazole Equilibrium of 2-Azido-1,3-benzothiazoles

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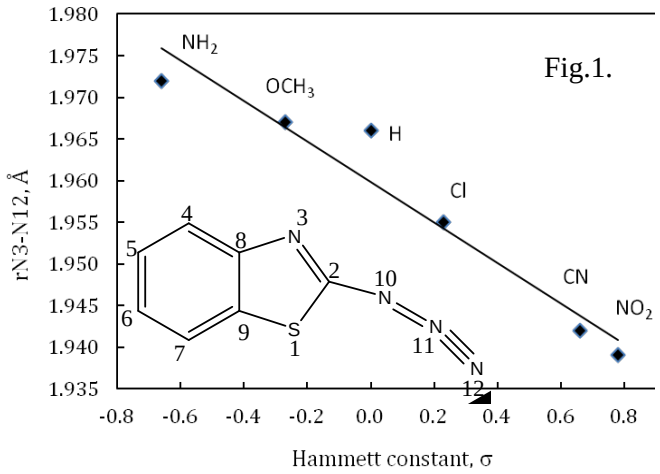
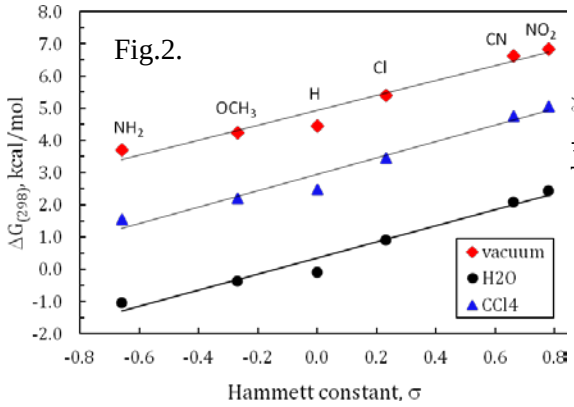
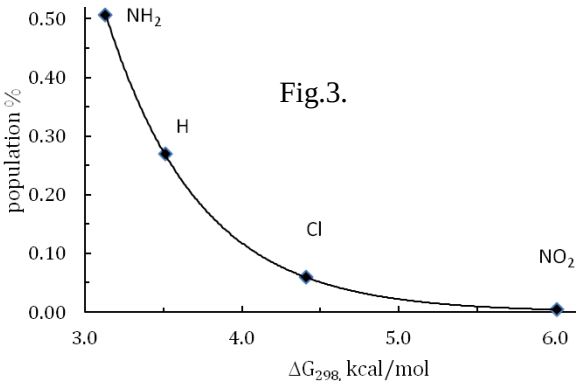
I. Abstract

Full geometry optimization using quantum chemical calculations at the *Ab initio* hybrid Density Functional Theory using at the B3LYP/6-311+G(d,p) have been performed to investigate the azide-tetrazole equilibrium of 2-azido-1,3-benzothiazoles. The electron correlation energy corrections were introduced by single-point calculations at MP2 and (CCSD(T)) levels. It was found that the electron donating groups enhance the stability of the tetrazole isomer while the electron-withdrawing groups favor the azide isomer. A plot of Hammett constant (σ) versus the length of the N3-N12 forming bond during cyclization is shown in the fig 1. The study confirmed that the relative stability of the tetrazole species can be maximized to a great extent by increasing the polarity of the solvent, and vice versa for the azide isomer which may be explained in terms of the relatively larger dipole moment of the tetrazole. The solvent and substituent effects on the free energy difference and population are shown in Fig. 2 and 3. The influence exerted by substituents of different electron donating or withdrawing strength on the geometries of cis-azide and tetrazole species is found to be insignificant. This may be due to the weak interaction between the azide group and a substituent through an aromatic ring. Moreover, the influence of substitution is expected to be better transmitted from the thiazole to the benzene part rather than in the opposite direction.







PIIa-37

A new perspective of solvation theory

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I. Introduction

In solution phase, a molecule experiences strong electrostatic field generated by all other molecules especially in polar solvent systems. In the last few decades, polarizable continuum model (PCM) becomes very popular, and a variety of hybrid method such as QM/MM has been developed. This is because the electronic structure of the molecule described with quantum chemistry, and the solvation structure around the molecule, which is governed by statistical mechanics, are coupled each other. In this regards, development of a new theory to unify these two treatments is vital to fundamentally understand chemical processes in solution phase. We have been developing RISM-SCF, which combines reference interaction site model (RISM) and ab initio molecular orbital theory. RISM-SCF has been successfully applied to numerous molecular phenomena including chemical reactions, chemical equilibria and so on [1].

II. An excited-state intramolecular proton-transfer reaction in ionic liquid

Recently developed RISM-SCF-SEDD incorporates the spatial electron density distribution (SEDD) of the solute molecule, and significantly expands the versatility of this hybrid approach [2]. In this contribution, we review RISM-SCF-SEDD method, together with recent applications for several chemical phenomena in room temperature ionic liquids (RTILs) [3]. In particular, an excited-state intra-molecular proton transfer (ESIPT) reaction of 4′-*N,N*-dimethylamino-3-hydroxyflavone in RTILs is focused on. The solvation dynamics of this system has been extensively studied with steady-state and time-resolved fluorescent spectroscopy. To incorporate the non-equilibrium solvation effects due to solvent fluctuation concomitant with the photo-excitation and proton-transfer process, we utilized a thermodynamic treatment proposed by Chong et al. The calculated absorption and emission energy are in good agreement with the experiments.

III. Statistical mechanics of solvation structure

The multi-center molecular Ornstein-Zernike (MC-MOZ) method [4], which is a highly parallelizable, statistical mechanical method to compute 3D solvation structure around large molecular systems such as proteins, and its related methods will be also briefly introduced.

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[2] D. Yokogawa, H. Sato and S. Sakaki, *J. Chem. Phys.*, **126**, 244504 (2007).
[3] (a) S. Hayaki, K. Kido, D. Yokogawa, H. Sato and S. Sakaki, *J. Phys. Chem. B*, **113**, 8227 (2009). (b) S. Hayaki, K. Kido, H. Sato and S. Sakaki, *Phys. Chem. Chem. Phys.*, **12**, 1822 (2010). (c) S. Hayaki, Y. Kimura and H. Sato, *J. Phys. Chem. B*, **117**, 6759 (2013).
[4] (a) D. Yokogawa, H. Sato and S. Sakaki, *J. Chem. Phys.*, **130**, 064111 (2009). (b) K. Kido, D. Yokogawa and H. Sato, *Chem. Phys. Lett*. **531**, 223 (2012). (c) K. Kido, D. Yokogawa and H. Sato, *J. Chem. Phys.*, **136**, 244502 (2012).

PIIa-38

The ring deformation of hydrogen maleate anion: A path integral molecular dynamics study

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I. Introduction

Low-barrier hydrogen bonds (LBHB), with short and strong bonds compared to typical hydrogen bonds, are suggested to play a key role in enzyme catalysis and proton transfer of biological systems. Hydrogen maleate anion $H(OOC\text{-}CH{=}CH\text{-}COO)^-$ (HM: Fig. 1) is a system which is widely used to study LBHB for the low proton transfer barrier in its intramolecular hydrogen bond (O···H···O). We employed *ab initio* path integral molecular dynamics (PIMD) simulation to understand the nuclear quantum effect on the out-of-plane ring deformation of HM and investigate the existence of a stable structure with ring deformation, which was suggested in experimental observation[1].

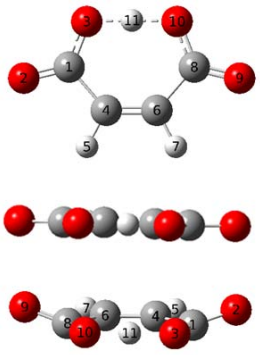

Fig. 1. HM and its planar structure and structure with ring deformation.

II. Experimental and computational method

All electronic structure calculations were performed using wB97XD/6-31G*. Additional diffused basis sets were employed for oxygen atoms. PIMD and AIMD simulations were carried out at 300 K with Nosé-Hoover chain thermostats to achieve canonical ensemble. We ran 100,000 step PIMD simulations with 16 beads using time steps of 0.1 and 0.15 fs for HM and DM, respectively. 200,000 step AIMD simulation was also executed using time step of 0.1 fs for HM.

III. Results and discussion

We first investigated the nuclear quantum effect on the proton transfer. In static calculation and classical *ab initio* molecular dynamics simulations, the proton in the hydrogen bond is localized to either oxygen atom. On the other hand, the proton is located at the center of two oxygen atoms in quantum *ab initio* PIMD simulations. The nuclear quantum effect washes out the barrier of proton transfer [2]. We next examined the nuclear quantum effect on the motion of HM and we successfully found a stable structure with ring deformation of hydrogen maleate, which was suggested in experimental observation [1]. Static *ab initio* electronic structure calculation found that the structures with ring deformation have very small proton transfer barrier compared to the planar structure. We suggest that the “proton transfer driven” mechanism is the origin of stabilization for the structure with out-of-plane ring deformation.

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PIIa-39

Cooperative Roles of Charge-Transfer and Dispersion Terms in Hydrogen Bonds of Water Clusters

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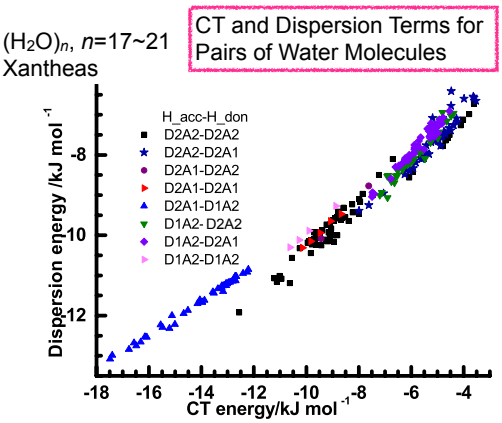
Hydrogen bonds between water molecules play an essential role in the structures, dynamics and thermochemical properties of liquid water and ices. So it is important to qualitatively and quantitatively characterize the hydrogen bonds between water molecules. In this presentation, the recent computational analyses of the hydrogen bonds in water clusters $(H_2O)_n$ up to n=25 are discussed. Table compares the relative binding energy of several isomers of n=16 and 20. Our perturbation theory based on the locally projected molecular orbital (LP MO PT) allows us to evaluate the charge-transfer and dispersion contribution to the hydrogen bond energy for every pair of water molecules in the clusters. The two terms are strongly correlated to each other for the hydrogen-bonded pair as is seen in the figure. Every water molecule is given index D*n*A*m*, where *n* is the number of donating hydrogen atoms (0~2), and *m* is the number of accepting hydrogen atoms (0~2). The strength of the hydrogen bonds is dependent on the types of pair D*n*A*m*←D*n'*A*m'*. The strong pair is found for the pairs D2A1←D1A2. This is previously known by the low-shifted calculated harmonic frequencies of OH stretching modes. The geometric distortion of a water molecule by the hydrogen bonding formation also depends on D*n*A*m*. A short summary of the theory, which is approximately free of basis set superposition error (BSSE), is also given.

Relative Energy (/kJ mol^{-1})of Isomers of $(H_2O)_{16}$ and $(H_2O)_{20}$ 1Hartree=2625.5kJ mol^{-1}

isomer	MP2	CCSD(T)	present method
$(H_2O)_{16}$ Etotal=-1216Hartree E_{Bind}=-664kJ mol^{-1}			
	aug-cc-pVTZ	aug-cc-pVTZ	aug-cc-pVDZ
4444-a	0.0	0.0	0.0
boat-a	-1.6	1.1	2.3
boat-b	-0.9	1.8	2.6
antiboat	-0.2	2.1	1.5
4444-b	1.9	2.3	2.8
$(H_2O)_{20}$ Etotal=-1521Hartree EBind=-853kJ mol^{-1}			
	MP2/aug-cc-pVDZ	MP2/aug-cc-pVTZ	aug-cc-pVDZ
edge-sharing	0.0	0.0	0.0
fused cubes	7.4	10.5	6.2
face-sharing	4.9	7.9	6.5
dodecahedron	52.3	46.7	47.6

Reference:1)JPC A114(2010)8697, 2)JCP 135(2011) 094101, 3)PCCP 14(2012)7787, 4) JPC A117(2013)6641



[1] Visiting Professor (2012-2014)
[2] Fellow (2008-2012)
[3] Emeritus Professor (2000-)

PIIa-40

BINDING $Pt^{IV}(DACH)Cl_4$ TO GMP AND FOLLOWED-UP REDUCTION OF PLATINUM LEADED TO FORMATION OF $Pt^{II}(DACH)Cl_2$

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Platinum complexes are well-known anticancer drugs. Recently also several other transition metal compounds were proven active both *in vitro* and *in vivo* experiments. There is an effort in recent medicine to replace cisplatin complexes by drugs with smaller side effects. Our calculations focus on the reaction of 5'-dGMP (2'-deoxyguanosine-5'-monophosphate) and 3'-dGMP with a platinum complex $Pt^{IV}(dach)Cl_4$ (dach=diaminocyclohexane) which leads to formation of active complex $Pt^{II}(dach)Cl_2$.

The first step of the explored mechanism is the substitution reaction where a new complex with coordinate-covalent bond between platinum and nitrogen N7 of guanine is formed releasing chloride particle. In the next step (besides a possibility of a phosphate cyclization reaction, which would terminate the process- green pathway) oxygen of phosphate group is transfer to C8 site of guanine forming 8-oxoguanine in the case of both 5'-dGMP (blue pathway) and 3'-dGMP (red pathway). The Pt^{IV} complex is within this step simultaneously reduced to Pt^{II} complex. Subsequently the Pt-N7 bond is broken (as shown in Fig. 1). The final products represent $Pt^{II}(dach)Cl_2$ and 8-oxo-GMP [1].

We studied geometry parameters of all species involved in this quite complex mechanism. The reaction course is considered from the thermodynamic point of view. The structures were optimized at the DFT level with B3LYP functional in basis set 6-31G* and PCM/UA0 solvation model. The energy parameters were determined using the single-point calculations at the DFT level B3LYP/6-311++G(2df,2pd) with DPCM/scaled-UAKS solvation model developed in our laboratory recently [2].

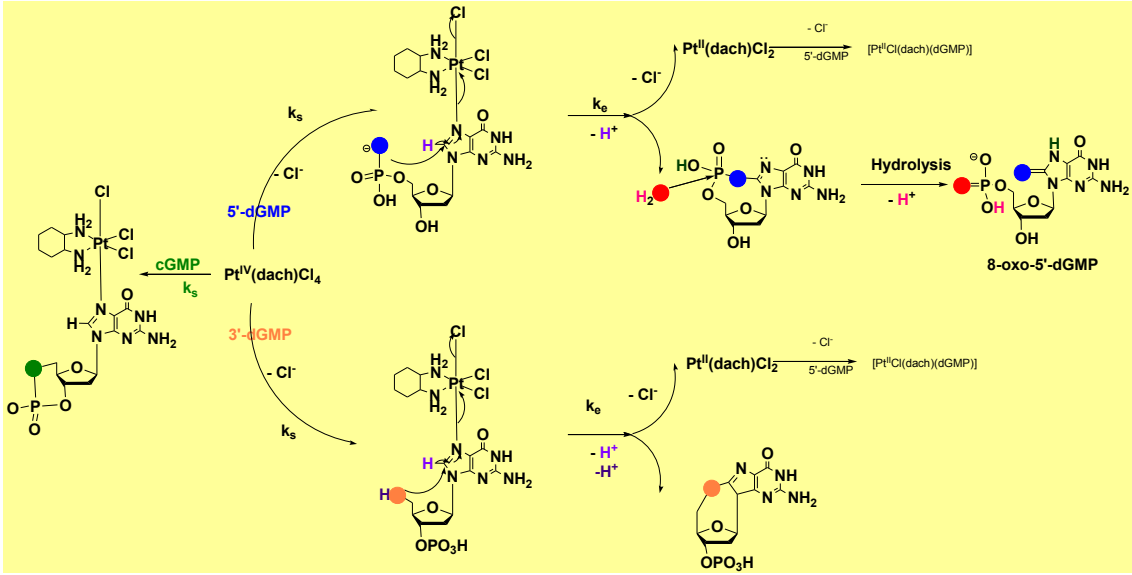

Figure 1: Scheme of the explored reaction

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PIIa-41

Non-Adiabatic Molecular Dynamics with FOMO-CAS-CI method

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Majority of the non-adiabatic molecular dynamical simulations are performed with the State-Averaged Complete Active Space Self-Consistent Field (CASSCF) method. While the accuracy of the method is questionable and the method should be always carefully benchmarked, its computational cost is for larger molecules still prohibitive. Furthermore, the CASSCF method is often unstable e.g. due to orbital rotations.

We have shown previously that the Complete Active Space Configuration Interaction method (CAS-CI) based on Floating Occupation Molecular Orbitals (FOMOs) represents a reliable and efficient approximation to the CASSCF method. The approach has been originally implemented in the semi-empirical[1] context and later also in its *ab initio* version.[2]

Here we test the suitability of the FOMO-CAS-CI approach for non-adiabatic simulations within the surface hopping framework. We show that the FOMO-CAS-CI is more stable and computationally much less demanding than the CASSCF approach with fully optimized orbitals. However, the numerical non-adiabatic coupling calculation[3] and numerical forces have to be used so far as the analytical gradients are not available.

We discuss the performance and application of the method for several molecules, investigating both the topology of the potential energy surface as well as the statistical characteristics of the non-adiabatic simulations.

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Acknowledgement: We acknowledge the support by the Grant Agency of The Czech Republic, project number 203/09/0422.