Abstracts of Poster Presentations, Sep. 4

4PP-01

Development and Implementation of a Manifestly Spin-Free State-Specific Multi-Reference Coupled Cluster (SS-MRCC) Theory Using a Multi-Exponential Type of Cluster Expansion

Rahul Maitra, Debalina Sinha and Debashis Mukherjee
Raman Center for Atomic, Molecular and Optical Sciences,
Indian Association for the Cultivation of Science,
Jadavpur, Kolkata,
India

In this poster, we present the formulation and the implementation of a spin-free State-Specific Multi-Reference Coupled Cluster (SS-MRCC) theory using a multi-exponential type of cluster expansion of the wave-operator Ω. Our Ansatz for Ω is a natural spin-free extension of the spin-orbital based Jeziorski-Monkhorst (JM) recipe. Although Datta and Mukherjee recently suggested an alternative spin-free generalization of the JM Ansatz, its structure is more involved. In contrast, our Ansatz is relatively simpler; it uses a terminating series, and it uses ordinary Wick algebra to generate the working equations. Just as in the case of the spin-orbital based SS-MRCC theory, there are redundancies in the cluster operators, which is exploited to ensure size-extensivity and avoidance of intruders via suitable sufficiency conditions. We demonstrate that our formulation is an appropriate compromise between the accuracy achieved by the more involved Datta-Mukherjee Ansatz leading to a finite expansion of the working equations and the unphysical and non-terminating Ansatz involving the pure exponential cluster operators with spin-free unitary generators.

4PP-02

Formulation and Implementation of a State-Specific Multi-reference Coupled-cluster (SS-MRCC) Theory Using an Internally Contracted Reference Function.

Debalina Sinha, Rahul Maitra and Debashis Mukherjee
Raman Center for Atomic, Molecular and Optical Sciences,
Indian Association for the Cultivation of Science,
Jadavpur, Kolkata,
India

In this poster we discuss the development and implementation of a State -Specific Multi-Reference Coupled Cluster theory which uses the common doubly occupied 'core' of the model functions as the vacuum for bringing in the effect of virtual excitations in the exact function of a many electron system. The Ansatz for the wave-operator Ω in our formulation is, unlike that in a Jeziorski-Monkhorst prescription, that of a single exponential type. Potential linear dependence of the cluster operators involving active orbitals are eliminated by choosing appropriately the linearly independent subspace of excitations. In this development, we make use of an Automatic Program Generation (APG) strategy using a Generalized Tensor Contraction Engine (TCE) developed by us. APG involves generation of the expressions for the working equations followed by the generation of the program.

4PP-03

Active CI space for ionized systems as defined by Koopmans' theorem

A.V. Novikov,[1] T.E. Prokhorov,[2] N.E. Polygalova,[2] A.V. Moskvin,[2] B.N. Plakhutin[1]
[1]*Laboratory of Quantum Chemistry, Boreskov Institute of Catalysis RAS, Russia*
[2]*Novosibirsk State University, Russia.*

According to the CI-based formulation of Koopmans' theorem (KT) in the ROHF method [1,2], the energy of an ion in a one-electron process $X \rightarrow X_j^{\pm}$ defined by Koopmans in the "frozen" orbital approximation, $E(X_j^{\pm}) = E_{frozen}(X_j^{\pm})$, is equal to the energy derived within the limited CI approach, i.e., $E_{frozen}(X_j^{\pm}) = E_{CI}(X_j^{\pm})$, with a special choice of the active CI space.

The active CI space defined by KT is specific for an ion under study and varies from a single excitation CI in the respective occupied subspace [1] for ions described in the ROHF method by a one-determinantal wave function to a combination of CI subspaces with different levels of excitation [3] for ions with arbitrary (non-integer) orbital occupancies. The main difficulty in constructing the desired CI space is a correct separation of configuration state functions (CSFs) corresponding to intruder states.

The paper presents a general and simple technique for constructing the active CI space satisfying the conditions of KT for arbitrary open-shell systems. A starting point is the CI matrix in the basis of Slater determinants derived with the ORMAS–CI method [4] implemented in the GAMESS suite of programs [5]. The key point of the algorithm is a two-step procedure for separating CSFs which contribute to intruder states. To illustrate the efficiency of the algorithm we compare KT estimates of the ionization potentials for a series of ions derived by the present CI method with the corresponding KT estimates derived by the canonical ROHF method [3,6] and with the respective experimental data.

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4PP-04

Open-Shell Coupled-Cluster Theory with Spin-Orbit Coupling

Fan Wang,[1] Zheyan Tu,[1] Jürgen Gauss[2]
[1]*College of Chemistry, Sichuan University, P. R. China*
[2] *Institut für Physikalische Chemie, Universität Mainz, Mainz, Germany*

Recently we proposed a two-component coupled-cluster (CC) approach for closed-shell molecules using relativistic effective core potential to treat relativistic effects and with spin-orbit coupling (SOC) included in the CC part. The total energy[1], analytic first[2] and second order derivatives[3] of this two-component CC approach were implemented at the CCSD and CCSD(T)) levels. Both time-reversal symmetry and point group symmetry are exploited in total energy and analytical energy gradients calculations. This approach is efficient and accurate in treating closed-shell molecules with SOC. However, SOC is generally more significant for open-shell systems. This two-component CC method can be extended readily to open-shell systems that are spatially non-degenerate. Otherwise convergence problem in solving CC equations will arise.

In present work, we developed the equation-of-motion method based on this two-component CCSD approach to circumvent this problem. We implemented EOM-CCSD to calculate excitation energies (EOMEE) and ionization energies (EOMIP) of closed-shell molecules. We can thus calculate open-shell excited states of a molecule with closed-shell ground state or both ground and excited states of open-shell molecules that can be reached by removing one electron from a closed-shell reference state. In this method, SOC can be included either at the CC part or only in the EOM equation. The latter approach, although not size-consistent, provide an economic way to treat SOC effects especially in EOMIP-CCSD and results show that it can lead to rather accurate results even for 5p element compounds. We further demonstrate implementation of analytic energy gradient for the two-component EOMEE-CCSD, which facilitates location of stationary points on excited state potential energy surfaces and harmonic frequencies of these stationary points.

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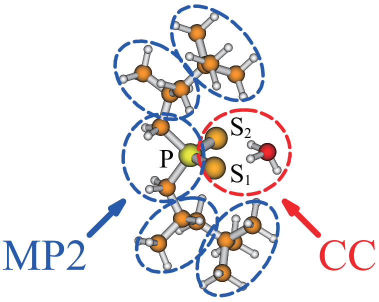
4PP-05

Multilevel extension of the cluster-in-molecule method for the chemical reactions of large molecules

Wei Li,[1,2] Piotr Piecuch[2]
[1]*School of Chemistry and Chemical Engineering, Nanjing University, China*
[2]*Department of Chemistry, Michigan State University, USA*

The linear scaling local correlation approach, termed "cluster-in-molecule (CIM)",[1-4] is extended to multilevel calculation,[5] which enables one to combine different quantum chemistry methods to treat the different regions in a large molecule. In the multilevel calculations, the reactive part of a large molecular system is treated by higher-level methods, such as coupled cluster (CC) with singes and doubes (CCSD) or the completely renormalized CC approach with singles, doubles, and noniterative triples, termed CR-CC(2,3). And the chemically inactive regions are treated by lower-level methods, such as the second-order Møller-Plesset perturbation theory (MP2). The key features of all CIM methods, such as the use of orthonormal localized orbitals and quasi-canonical molecular orbitals (QCMO), the and coarse-grain parallelism, can be preserved. Our illustrative calculations show that the multilevel CIM-CC/MP2 reduces the already relatively low costs of the singe-level CIM-CC while keeps similar accuracy.[5]



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4PP-06

Multireference Perturbation Theory Can Predict a False Ground State

Henryk A. Witek,[1] Cristopher Camacho,[1] Renzo Cimiraglia[2]
[1]*Department of Applied Chemistry and Institute of Molecular Science,National Chiao Tung University, 30010 Hsinchu, Taiwan*
[2] *Dipartimento di Chimica, Universita di Ferrara,Via Borsari 46, I-44100 Ferrara, Italy*

We have recently discovered [1, 2] that popular variants of multireference perturbation theory (CASPT2 and MRMP) can predict a false ground state for a remarkably simple chemical system: the scandium dimer. The MRMP and CASPT2 calculations on Sc_2 using a reduced valence (12o, 6e) active space were found to suffer severely from intruder states (i.e., the quasi-degeneracies in the spectrum of the zeroth-order Hamiltonian); employing intruder state removal techniques helped us to obtain smooth and continuous potential energy curves. Unfortunately, the shape of the curves and their energy order depended strongly on the magnitude of the shift parameter σ; for small values of σ, MRMP and CASPT2 predicted that the ground state of Sc_2 is $^3\Sigma_u^-$, while for large values of σ, they predicted $^5\Sigma_u^-$. Analogous calculations performed with NEVPT2—a recent variant of multireference perturbation theory free from the intruder state problem owing to a partially bielectronic definition of the zeroth-order Hamiltonian—showed clearly [3] that the ground state is $^5\Sigma_u^-$. Our calculations clearly show that CASPT2 and MRMP used in conjunction with the intruder-state removal techniques are capable of predicting a false ground state even for very simple molecular systems. This finding casts serious doubts on the validity of the shift techniques in the framework of multireference perturbation theory and shows that this direction of development can be a dead-end street.

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4PP-07

Antisymmetric product of strongly orthogonal geminals (APSG): Its acceleration and extension to open-shell systems

Moto Tarumi,[1] Masato Kobayashi,[1,2] Hiromi Nakai[1,3,4]
[1]*School of Advanced Science and Engineering, Waseda University, Japan*
[2]*Institute for Molecular Science, Japan*
[3]*Reserch Institute for Science and Engineering, Waseda University, Japan*
[4]*CREST, Japan Science and Technology Agency, Japan*

I. Introduction

Antisymmetric product of strongly orthogonal geminals (APSG) method [1,2] is a wave-function theory that can effectively treat the static electron correlation. In the APSG method, the all-electron wave function is constructed as the antisymmetric product of two-electron wave functions, called geminals. However, there are several problems in this method that should be overcome for its practical applications. First, the APSG procedure occasionally faces on the convergence problem. In this study, we introduced the direct inversion in the iterative subspace (DIIS) method into the APSG optimization process. In addition, we extended the APSG method to open-shell system calculations by using one-electron orbitals for the open-shell part, as Rassolov [3] introduced into his geminal theory.

II. Acceleration with DIIS method

In the APSG method, a geminal ψ is composed of mutually exclusive natural orbitals φ,

$$\psi^I(x_1,x_2)=\sum_{m\in I} C_m^I \varphi_m(r_1)\varphi_m(r_2)\,{}^1\vartheta(1,2), \qquad (1)$$

where ${}^1\vartheta(1,2)$ is the antisymmetric spin function, and natural orbitals φ are represented as a unitary transformation of orthonormal orbitals ϕ with $\mathbf{T}$, which is optimized with the Newton-Raphson method until the orbital gradient $\mathbf{g}$ becomes zero. $\mathbf{C}$ is the coefficient matrix determined by the local Schrödinger equation for each geminal. In this study, DIIS method is introduced into the optimization process of $\mathbf{T}$. This method reduces the computational time for the APSG calculation to 30%-50% of the original.

III. Extension to open-shell systems

In open-shell systems, we define the APSG wave function with two-electron geminals and one-electron natural orbitals as follows:

$$\Phi_{\mathrm{APSG}} = \hat{A}\left[\psi^1(x_1,x_2)\psi^2(x_3,x_4)\cdots\psi^{N_\mathrm{C}/2}\left(x_{N_\mathrm{C}-1},x_{N_\mathrm{C}}\right)\varphi_1\left(x_{N_\mathrm{C}+1}\right)\cdots\varphi_{N_\mathrm{O}}\left(x_{N_\mathrm{C}+N_\mathrm{O}}\right)\right], \qquad (2)$$

where $\hat{A}$ is antisymmetrization operator, and N_C and N_O mean numbers of electrons in closed and open shells, respectively. We implemented this method into GAMESS program, and have succeeded in describing the radical dissociation of the OH molecule.

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4PP-08

Efficient algorithm of the transcorrelated method for periodic systems - feasible wavefunction-based approach for solids -

Masayuki Ochi,[1] Keitaro Sodeyama,[2,3] Rei Sakuma,[3,4,5] and Shinji Tsuneyuki[1,6]
[1]*Department of Physics, The University of Tokyo, Japan*
[2]*WPI International Center for Materials Nanoarchitectonics, NIMS, Japan*
[3]*Japan Science and Technology Agency, CREST, Japan*
[4]*Graduate School of Advanced Integration Science, Chiba University, Japan*
[5]*National Institute of Advanced Industrial Science and Technology, Japan*
[6]*Institute for Solid State Physics, Japan*

In *ab-initio* electronic structure calculations of solids, density functional theory (DFT) is presently the most popular method since it gives us satisfactory results in many cases with relatively low computational cost, while it is difficult for the DFT-based methods to improve their accuracy systematically. On the other hand, traditional wavefunction-based approaches have systematic ways to improve their accuracies although it is not easy to apply them for solids because of their heavy computational costs.

The transcorrelated (TC) method [1-4] is a wavefunction-based approach applicable to solids in terms of the computational cost. In this method, the total wavefunction is approximated as a product of the Jastrow factor and the Slater determinant.

$$\Psi = F\Phi, \qquad F = \exp(-\sum_{i \neq j} u(x_i, x_j)) \text{: Jastrow factor, } \; \Phi \text{: Slater determinant}$$

Next the Hamiltonian is similarity-transformed by the Jastrow factor,

$$H\Psi = E\Psi \Leftrightarrow (F^{-1}HF)\Phi = E\Phi .$$

and we solve an SCF equation constructed like the HF method. It is a remarkable feature that we can optimize one-electron orbitals in the Slater determinant with relatively low computational cost comparing with other methods utilizing the Jastrow-Slater-type wavefunctions, e.g., Variational Monte Carlo method.

In this study, we introduce our new efficient algorithm, which reduces a computational cost of the TC method to the same order of magnitude as the HF method. Moreover, we show the computational time, accuracy, and other properties of the TC method, calculations for which have been enabled by our efficient algorithm.

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4PP-09

Numerical analysis for eigenvalue problems in quantum mechanics and atomic structure calculations

Hideaki Ishikawa
Home, Hadano-shi, Kanagawa-ken, Japan

I. Introduction

In order to get fruitful insights into structures and electronic states of atoms, molecules and solids based on first-principles, we have to carry out highly accurate and fast numerical calculations. Numerical methods widely used thus far have provided 8-digits and 5-digits accuracy at most, for atomic structure and molecular orbital calculations, respectively. We have to realize high accuracy with more than or equal to 13-digits and 10-digits accuracy for atomic structure and molecular orbital calculations, respectively. We report here a new set of highly accurate and fast methods of numerical solutions for eigenvalue problems in quantum mechanics and atomic structures.

II. Numerical methods of calculation

In the one-body problems we solve the eigenvalue problem of the Schrödinger equation for a given potential [1-4]. For one-dimensional problems, we established highly accurate methods of numerical calculation for interpolation, derivatives, integration, and initial-value problems of the second-order ordinary differential equations (ODEs). We realized highly accurate methods of numerical solution for the eigenvalue problems by using the discretized matrix eigenvalue method and the shooting method. For central-force-field problems we developed a method of solution for ODEs around singularities (power and asymptotic series expansions) and solved radial eigenvalue problems by using the shooting method.

In the many-body problems, we solve the eigenvalue problems for the Schrödinger equation in the mean field approximation. For the atomic structure calculations, we developed a new set of highly accurate numerical methods of indefinite integrations and of solutions for the initial-value problems of the first-order ODEs for calculating potentials. In addition, we solved self-consistently the radial eigenvalue problem and potential calculation [5].

III. Results

We obtained from 13- to 15-digits accuracy for the eigenvalues. The maximum absolute error of the eigenfunctions was of order less than 5×10^{-13}.

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An Overlap Fitted RIJCOSX Theory

Róbert Izsák,[1] Frank Neese[1]
[1]*Lehrstuhl für Theoretische Chemie, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Germany*

The acceleration and extension of present standard theoretical methodologies for large molecular systems is in the forefront of modern Quantum Chemical research. The RIJCOSX algorithm[1] addresses the problem of integral evaluation in particular. This algorithm combines the advantages of the Split-RI-J approximation[2] for the evaluation of Coulomb integrals, and follows closely the pseudo-spectral approach of Friesner[3] for the exchange integrals. The "chain of spheres" (COSX) algorithm approximates two electron integrals by performing analytic integration with respect to the coordinates of only one of the two electrons, whereas for the remaining coordinates integration is carried out numerically through the evaluation of basis functions over grid points to reduce the cost of the calculation. In the present work, we attempt to minimize the effect of numerical errors in the COSX procedure, which makes it necessary to use rather large grids to achieve chemical accuracy. The idea based on the work of Friesner, and futher explored by Ten-no, is that we look for a solution of the equation:

$$\mathbf{S} = \mathbf{Q}\mathbf{X}^T$$

where $\mathbf{S}$ is the analytic overlap matrix of basisfunctions, $\mathbf{X}$ contains basisfunction values evaluated over the grid, and $\mathbf{Q}$ is therefore a matrix which makes the numerical evaluation of overlap integrals exact. Subsequently, $\mathbf{Q}$ can be used to evaluate the exchange integrals in the COSX algorithm. This results in a reduction of grid sizes necessary for chemical accuracy, and a corresponding 30% speed up over the original RIJCOSX procedure for single point energy and gradient calculations. The new method is referred to as the overlap fitted RIJCOSX theory.

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4PP-11

Development and Applications of Theoretical Methods for Solvated Molecular System

Hirofumi Sato
Department of Molecular Engineering, Kyoto University, Japan

I. Introduction

Recent development of experimental technique makes it increasingly clear that the electronic structure of a molecule is significantly changed when it is dissolved into polar solvent. This means electronic structure, which is treated by quantum chemistry, and solvation structure, which is governed by statistical mechanics, are coupled each other. In this regards, development of new theory that can bridge between these two methodologies is indispensable to properly understand ordinary chemical processes. In the last few decades, various types of hybrid method, such as polarizable continuum model (PCM) and QM/MM, have been developed and applied to a variety of chemical phenomena [1].

II. RISM-SCF-SEDD method and its applications

We have been developing RISM-SCF, which combines two ab initio methods in theoretical chemistry: one is the reference interaction site model (RISM), and the other is ab initio molecular orbital (MO) theory. The method determines electronic structure of a solute molecule and statistical solvent distribution around it in a self-consistent manner. It is a remarkable advantage of RISM-SCF method that provides microscopic solvation structure based on the statistical mechanics. RISM-SCF-SEDD [2] is regarded as a new generation method and significantly expands the versatility of the RISM-SCF family. The method has been successfully applied to numerous molecular phenomena such as chemical reactions and equilibria.

In this contribution, we will review our theoretical methods together with recent applications for several chemical phenomena in solution phase including chemical reactions in ionic liquids, electronic excitation of solvated molecules and so on [3].

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4PP-12

A new procedure for the calculation of electron transfer coupling matrix element

Mitsuo Shoji,[1] Kyohei Hanaoka,[2] Moonyoung Yang,[2] Daiki Kondo,[2]
Katsumasa Kamiya,[2] Kenji Shiraishi[2]
[1] *Center for Computational Science, University of Tsukuba, Japan*
[2] *Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan*

Electron transfer (ET) steps are critical for many biological processes such as photosynthesis, respiration and many enzyme reactions. Characterization of ET reactions is of great importance in a variety of chemical and biological systems. One of the key factors in determining the ET rate is electron transfer coupling matrix, *T* value. For symmetric systems, the *T* value can be easily evaluated from the orbital energy gap, however, this procedure is limited to symmetric systems.

In this study, a new procedure for the *T* value evaluation for asymmetric systems is proposed through the utilization of the orbital localization method. This new procedure is applied to three typical ET cases, phenoxyl radical-phenol, DNA sequences, and copper containing nitrite reductase (CuNiR).

It is demonstrated that *T* values are properly evaluated. Other related parameters, state energy gap (Δ*E*) and localization index (*L*), and localized molecular orbitals are very useful to characterize the electron transfer reactions and redox-active orbitals (Fig.1). This new approach can be utilized for other general ET reactions.

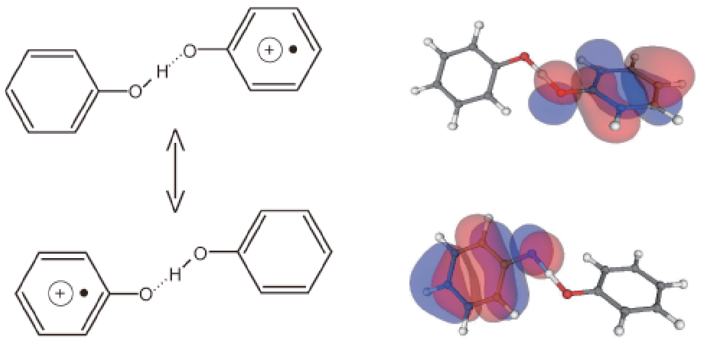

Fig. 1 internal electron transfer in a phenoxyl radical-phenol system.

4PP-13

Charge Transfer Complexes of Dihalogen Molecules: From Weak Intermolecular Interactions to Dative Bonds

Ye Cao[1], Ming Wah Wong[1]

[1]*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543*

High-level ab initio theory, at CCSD(T)/aug-cc-pVTZ//mp2/aug-cc-pVDZ level, was employed to study systematically the intermolecular complexes of dihalogen molecules with various donors, such as ammonia and trimethylamine. This type of charge transfer complexes is categorized by Mulliken to be the 'associative-dissociative' complex. The dihalogen complexes studied here are characterized by a wide and almost continuous span of binding energies, from nearly zero to more than 20 kcal/mol. In the case of $F_2\cdots PMe_3$ complex, it has a larger binding energy than that of BH_3NH_3, a prototypical example of dative bond. The transition from a weak intermolecular interaction to a dative bond is evidenced in this series of dihalogen complexes.

SAPT and NBO analyses were employed to understand the nature of binding interactions. In the weakly bound complexes, the electrostatic interaction plays a dominant role. As the binding becomes stronger, induction, mostly charge transfer, becomes more important. Both electrostatic interactions and charge transfer have major effects on weakening the dihalogen bond and lead to the formation of an intermolecular dative bond for the strongly bound complexes.

The formation of a strong dihalogen complex can be considered as a chemical reaction that breaks a dihalogen bond and forms a new bond simultaneously. Born-Habor cycles were used to shed light on the process of the chemical reaction. Constrained DFT, CASSCF calculations were also performed to understand the curve crossing of reaction and product states, and other possible intermediate states. The charge transfer state $[D^+(XY)^-]$ is shown to be important in the strongly bound dihalogen complexes.

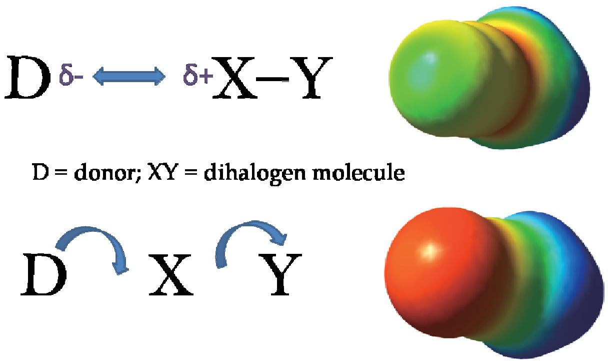

Figure 1. Illustration of the transition from electrostatic interaction to charge transfer in the complexes with dihalogen molecules

4PP-14

Cracking Reaction of C2-C4 Alkanes Sorbed in ZSM-5

Kanjarat Sukrat,[1] Daniel Tunega,[2,3] Adelia J.A. Aquino,[2] Hans Lischka,[2] Vudhichai Parasuk[1]

[1]*Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Rd., Patumwan, Bangkok, 10330 Thailand*

[2]*Institute of Theoretical Chemistry, University of Vienna, Währingerstraße 17, A-1090, Vienna, Austria*

[3]*Institute of Soil Research, University of Natural Resources and Applied Life Sciences, Peter-Jordan-Straße 82, A-1190, Vienna, Austria*

Quantum chemical methods were performed by various cluster models to determine adsorption energies and reaction barriers (activation energy) for cracking reactions of small alkanes (C2-C4) in zeolite ZSM-5. The characteristics and behaviors of the alkane molecules inside ZSM-5 were revealed from the optimized geometries of adsorption and transition state (TS). Two protonated positions on the C-C bond of alkanes of the zeolitic proton (pathway 1 and 2) were studied. Bond distances between breaking carbon atoms and proton can be used to predict the outcome of products. Effects such as cluster size, zero point energy, basis set, and electron correlation have also been monitored. An extrapolation technique incorporating such effects has been proposed. The cluster size showed largest impact on both adsorption energy and reaction barrier, while other effects were small. The reaction barrier of the cracking reaction suggests pathway 2 is more favorable than pathway 1. Computed energies agree well with experiments.

4PP-15

Giant SAC-CI method: Application to proteins

Tomoo Miyahara and Hiroshi Nakatsuji
[1]*Quantum Chemistry Research Institute (QCRI), Kyodai Katsura Venture Plaza, North building 106, 1-36 Goryo-Oohara, Nishikyo-ku, Kyoto 615-8245, Japan*
[2]*Japan Science and Technology Agency, CREST*

The SAC/SAC-CI method is a useful established method for studying ground, excited, ionized and electron attached states of molecules [1-3]. It is widely distributed through Gaussian09 [4]. However, it is difficult to calculate large molecules such as proteins and crystals etc. Therefore, we are developing a new method by extending the SAC/SAC-CI methodology to giant molecular systems like molecular crystals etc [5]. We call it Giant SAC/SAC-CI method. Recently, this method is designed to be much faster than the original method with the same chemical accuracy.

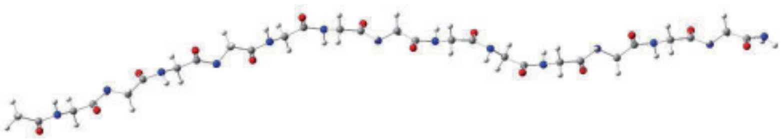

Figure 1. The structure of glycine polypeptide

We developed the Giant SAC-CI program for non-periodic systems and applied to glycine polypeptide (Fig. 1) as a test molecule. Glycine has no D,L isomer and is optically inactive, because glycine is the simplest amino acid and does not have any asymmetric carbon atom. However, glycine polypeptide is optically active because the symmetry is broken when glycine is linked with peptide bond. Therefore, we calculated the excitation energies and rotatory strengths of polypeptide.

We compared the results obtained from the Giant SAC-CI method with the Gaussian 09 (standard) SAC-CI method. The differences of the excitation energies were very small and the Giant SAC-CI could provide the same accuracy as the standard SAC-CI. Nevertheless, the computational cost was much reduced to one-seventh. We can calculate more efficiently, when the system is larger. We will present the result of other proteins

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4PP-16

Screening of Metals for CO_2 capture in MOF with Open-Metal site through the First-Principle Study

Joonho Park[1], Sang Soo Han[2], and Yousung Jung[1]

[1]Graduate School of EEWS (WCU), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

[2]Center for Nanocharacterization, Korea Research Institute of Standards and Science, Daejeon 305-340, Korea

I. Introduction

The emission of the greenhouse gas mostly from the fossil fuel induces severe damages on the climate and ecology of the planet. Worldwide efforts to reduce carbon in the atmosphere are going on in the industrial and academic fields. Metal-Organic Framework (MOF) is promising material to capture carbon in several aspects that it can contain carbon voluminous scale and the restoration energy is quite small compared to Monoethanolamine (MEA) used widely in the plant.

II. Abstracts

The capability of metals to adsorb CO_2 with reference to the MOF-74 was studied. MOF-74 structure has the open metal site and the metal directly binds to CO_2. All the metals in the first transition metal series together with Mg and Ca was investigated using first principle method equipped in VASP. Though the Mg-MOF-74 has been known to have high adsorption enthalpy, Ca, Ti, and V are shown to have better capabilities for CO_2 adsorption. Among them, Ti is most powerful adsorbent with 5kJ/mol higher than Mg. The tendency of adsorptivity is consistent with metals in the order of Mg, Ni, Zn, Co, and Cu as reported earlier. Though the absolute magnitude of adsorption enthalpy is smaller than experimental value, DFT shows a reliable data to measure the adsorption qualitatively. The effect of cell relaxation (MOF+CO_2) and the dispersion energy between the CO_2 molecules (RIMP2/BSSE, QChem) contribute less than 2kJ/mol to the adsorption enthalpy, respectively. All the bindings of CO_2 on the open metal sites belong to physisorption regime.

III. Table and Figure

MOF74-Mg	Experiment[1]	Simulation[1]	Present
BE (kJ/mol)	47	20.2	20.8
latt. const. (hexagonal)	a =26.02 c = 6.72		a =26.11 c = 6.91

Table 1. The comparison of binding energy of CO2 and the structure constants of hexagonal MOF-74

[1] Hui Wu et al. JPCL, 1 (2010)

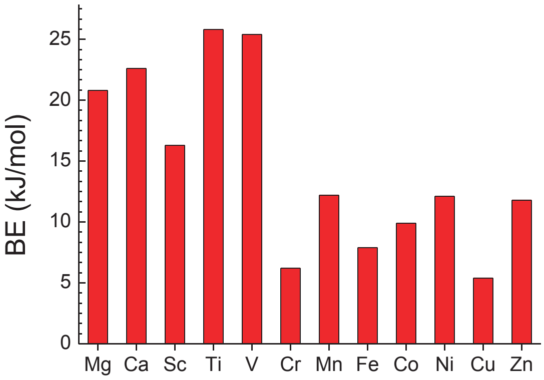

Fig. 1 The binding energy of CO2 on the open-metal site of MOF-74

Combination of spin-restricted and spin-projected calculations for a geometry optimization of large biradical systems

Yasutaka Kitagawa, Toru Saito, Yusuke Kataoka, Natsumi Yasuda, Hiroshi Hatake,
Toru Matsui, Takashi Kawakami, Shusuke Yamanaka, Mitsutaka Okumura and
Kizashi Yamaguch
Graduate School of Science, Osaka University, Japan

With the recent progress in quantum chemistry, we can calculate electronic structures, energies and energy derivatives of large molecules by the first principle methods. A broken-symmetry (BS) (or an unrestricted: U) method approximately but easily corrects the static correlation at the lower computational costs. However the BS method involves a serious problem called a spin contamination error (SCE). For the problem, our group has proposed a spin-projection method to eliminate the SCE from the energy derivatives based on Yamaguchi's approximate spin projection (AP) procedure [1-4]. By the AP method, one can optimize the geometry of the biradical systems without SCE at the costs of the BS level calculations. However one must carry out 6*N* (*N = optimizing atoms*) times single-point calculations previous to the geometry optimization because it uses a numerical derivative for $d\langle S^2\rangle/d\mathbf{R}$ values. In addition, it also requires both the low-spin and the high-spin state calculations during the geometry optimization. Therefore the reduction of the computational costs is a problem of the AP method for the optimization of the larger biradical systems such as a binuclear metal complex (e.g. Figure 1). In this study, we attempt to combine the AP method and the spin-restricted (R) methods, i.e. two-layer QM/QM' approach based on ONIOM method. In the method, the effect of the outer-ligands is included by the restricted method whilst an energy gradient of the core is calculated by the AP method using a reduced (small) model. The detail about the method and results are illustrated in the presentation.

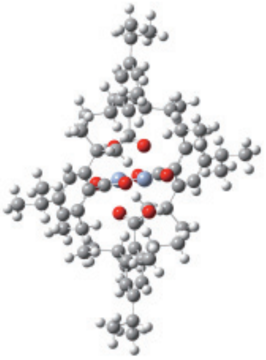

Fig. 1
$Cr_2(O_2C(CHMe_2)_3)_4$

References

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4PP-18

Norm-conserving stochastic Hartree-Fock calculation on electronic states in molecules

Tatsuji Sano
Department of Engineering Sciences, The University of Electro-Communications, Japan

It is a difficult computational problem to solve the Schrödinger equation for a many-electron system. Therefore, development of accurate and computationally efficient methods for calculating the ground and excited electronic states of molecules is one of the biggest challenges in the theoretical chemical physics. Generally, exact strategies for many-body problems need computational costs scaling up exponentially with the number of electrons. Recently Juillet and Chomaz proposed a stochastic time-dependent Hartree-Fock approach in which the quantum N-body dynamics with two-body interactions is exactly decomposed into the average of N one-body stochastic evolutions and thereby the usual exponential scaling of computational costs can be eliminated [1]. However, the norms of the one-body stochastic wavefunctions grow exponentially. This is related to the sign or phase problem which occurs in the auxiliary field Monte-Carlo approach. In order to overcome the above drawback, an exact one-body decomposition of time-dependent Schrödinger equation for a many-electron system in which one-body wavefunctions obey Ito-type stochastic time-dependent norm-coserving equations has been derived and applied to calculation of the low energy spectrum in Helium atom [2]. In this study we apply the norm-conserving stochastic time-dependent Hartree-Fock method to calculation of the electronic ground and excited states in molecules. The N-electron wavefunction is expressed in terms of an ensemble average over stochastic Slater determinants. The Coulomb (two-body) interaction part of the Hamiltonian is represented as a sum of products of one-body operators and treated as a source of noise. The stochastic differentials of complex general spin-orbitals are determined by Ito-type stochastic wave equations which conserve norm but do not orthogonality. Numerical integration was performed with the stochastic generalization of the fourth order Runge-Kutta scheme. The energy spectrum can be expressed as the Fourier transform of the time auto-correlation function. From another point of view we try to extend the norm-conserving stochastic Hartree-Fock interpretation of the evolution process to imaginary time in order to obtain the correlated N-body ground state in the limit of large imaginary time. Numerical results of our test calculations will be reported.

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4PP-19

Dispersion Energy of van der Waals Complex; Approximate Evaluation with Pair-wise Correlation Effect

Milind M. Deshmukh,[1] Shigeyoshi Sakaki[1]
[1]*Fukui Institute for Fundamental Chemistry, Kyoto University, Japan*

I. Introduction: Accurate estimation of dispersion energy is essential for study of van der Waals (vdW) complex; however such estimation is computationally demanding especially when many monomers are involved. To reduced computational cost, basis set extension methodologies [1] and many-body decomposition schemes were proposed [2]. Although these methods are effective to certain extend, the MP2, MP3 and CCSD(T) levels are computationally demanding even with basis set of medium size.

II. Computational Details: We propose new approximate equation for accurate estimation of dispersion energy based on the idea that molecular orbitals of dimer system AB are little different from those of AB moiety in total vdW complex. We analytically showed that the total dispersion energy of vdW complex can be accurately evaluated as sum of the dispersion contribution of all possible dimers in vdW complex. Based on this, the binding energy (BE) of vdW complex is calculated as;

$$\mathrm{BE} = \mathrm{BE(HF)} + \sum_{A>B} \{\mathrm{BE}_{\text{A-B}}(\text{correlated level}) - \mathrm{BE}_{\text{A-B}}(\mathrm{HF})\}, \qquad (1)$$

where A and B are interacting monomers. The first term is usual Hartree-Fock (HF) binding energy. The second term is sum of the difference in two-body binding energy between correlated and HF level. The MP2 and MP2.5 methods [3] were employed. The aug-cc-pVTZ and aug-cc-pVQZ basis sets were used.

III. Results and Discussion: Binding energies of various vdW complexes generated using dimers reported in S22 data set, are evaluated. Highly accurate binding energies are obtained with proposed equations; See Figure 1. Also, precise minimum on PES is obtained with these equations (Table 1). Application to transition metal complexes suggests that these equations are useful to study aurophilic interactions.

Table 1: Comparison of minimum position (Å) on MP2.5 PES between reference ($R_{ref.}$) and by the approximate equations ($R_{aaprox.}$).

Complexes	Minimum position	
	$R_{approx.}$	$R_{ref.}$
CO_2-trimer	3.541	3.533
CS_2-trimer	4.318	4.326
Acetylene-trimer	1.742	1.741
Water-trimer	2.420	2.420

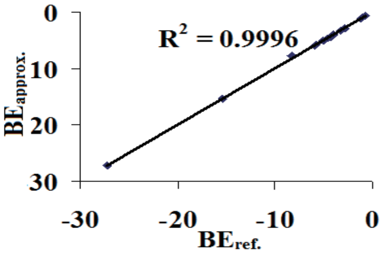

Figure 1: Comparison of BE calculated between the reference value ($BE_{ref.}$)[a] and approximate eq. (1).

[a] $BE_{ref.} = E_t(M_i : M_j : ...) - \sum_{M_i} E(M_i)$

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4PP-20

OpenMP/MPI hybrid parallelization of GAMESS

Hiroaki Umeda,[1,2] Mitsuhisa Sato,[2]
[1]*Institute for Molecular Science, National Institute of Natural Sciences, Japan*
[2]*Center for Computational Sciences, University of Tsukuba, Japan*

I. Introduction

Hybrid parallelization with OpenMP and MPI becomes unavoidable programing model for the recent HPC computer system, which has massive processor cores. We have modified GAMESS program [1] with OpenMP/MPI hybrid parallelization model to acquire large fragment molecular orbital (FMO) calculation [2] on the massively parallel HPC system.

II. GAMESS and Parallelization

The GAMESS program is parallelized with distributed data interface (DDI) as a message-passing API to realize remote memory access (RMA) operations. Using RMA functions of DDI library, we can easily parallelize program with dynamic load-balancing scheme, where small tasks are evenly distributed through a single global counter. For a massively parallel computer, this global counter could become a bottleneck of parallelization efficiencies, thus we have evaluated the performance of various DDI implementations.

Parallelization with OpenMP has performed only for FMO calculation with RI-MP2. Because the FMO calculation treats relatively small fragments or fragment-pairs, we have implemented both direct and in-core scheme for HF calculation. The most of RI-MP2 calculation spend CPU time for matrix-matrix multiplies with DGEMM routine in BLAS library; therefore the OpenMP parallelization is easily obtained using OpenMP-supported BLAS library.

III. Benchmark Results

Benchmark calculations were performed on the T2K Tsukuba system [3] in University of Tsukuba. Comparison with various DDI implementations shows the DDI implementation with ARMCI library is the best performance for HF calculation, where main communication bottleneck is the access to the global counter. In addition to the implementation of DDI, we found the importance of the processor affinity. Large benchmark calculations of FMO/RI-MP2 method were also performed with 10,240 processor cores with/without OpenMP parallelization. The OpenMP/MPI hybrid parallel execution shows better performance than the flat MPI parallel execution.

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4PP-21

Theoretical Study on the Working Mechanism of Stilbene Light-Driven Molecular Rotary Motor

Fengyi Liu, Keiji Morokuma
Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

Artificial synthesized light-driven molecular motors, which convert external energy to mechanical force, have been widespread in the past decade. We carried out the CASSCF/CASPT2 calculations to explore the rotary potential energy surface of a geometrically overcrowded, chiral stiff-stilbene molecular motor ((*2R,2R*)-2,2′,7,7′-tetramethyl-1,1′-bis(indanylidene), see Figure 1), as well to characterize the interaction between the PESs of the involved electronic states. The reaction paths of the two photo-initiated *cis-trans* (or *E/Z*) isomerization steps, namely, *[P,P]-cis* → *[M,M]-unstable-trans* and *[P,P]-trans* → *[M,M]-unstable-cis* have been explored. The minimal energy reaction paths (MEPs) of these two processes are parallel on the PESs and show remarkably steep slope, which drives C=C bond rotate unidirectionaly. The bias on the excited-state MEPs are caused by the asymmetric substituents on the "fjord" region as well as that between the phenyl moieties. The reactions are supported to flow a three-state, multi-modes mechanism: The excited molecules on 1B state first cross the sloped 1B/2A conical intersections (1B/2A CIs), then preferentially approach one of the two 2A/1A CIs flowing two cooperative torsional reaction modes. The findings of the present study are expected to shed light on understanding the working mechanism of the stilbene molecular motor and to rationalize the unidirectionality of the photo-initiated C=C rotation processes.

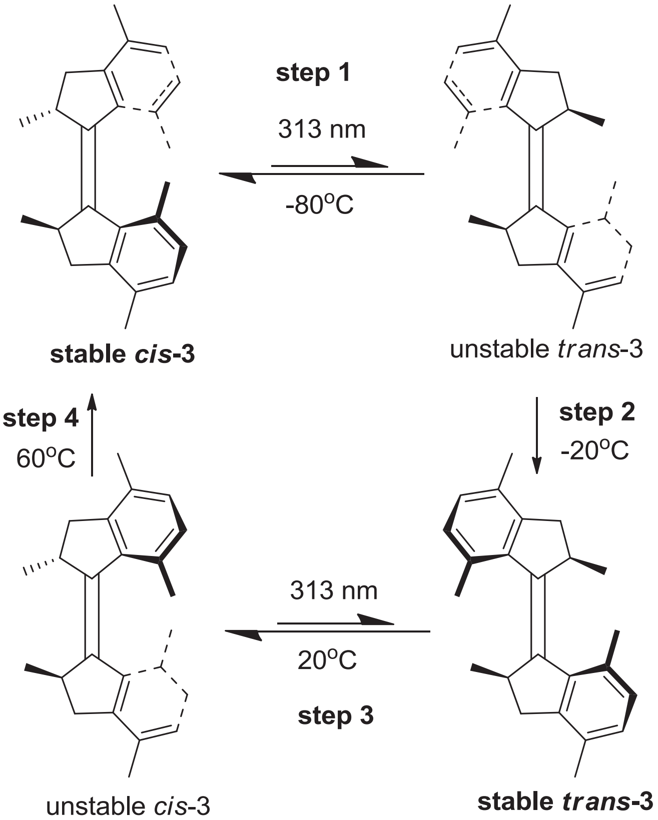

Figure 1. Four-step rotation scheme in stiff-stilbene light-driven molecular rotary motor 3 (Ref 1).

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4PP-22

Massively parallel second-order Møller–Plesset perturbation calculations based on divide-and-conquer method

Michio Katouda,[1] Masato Kobayashi,[1,2] Hiromi Nakai,[2,3,4] Shigeru Nagase[1]
[1] *Institute for Molecular Science, Japan*
[2] *School of Advanced Science and Engineering, Waseda University, Japan*
[3] *Research Institute for Science and Engineering, Waseda University, Japan*
[4] *CREST, Japan Science and Technology Agency, Japan*

I. Introduction

The divide-and-conquer (DC) method is the promising tool for the density functional theory (DFT) and Hartree-Fock (HF) calculation of large molecules. In the DC method, a target system is spatially divided into small fragments and then the energy and the properties are evaluated by accumulating contributions of fragmented systems. The DC method has been extended to the second-order Møller–Plesset perturbation (MP2) method (DC-MP2) [1,2]. DC-MP2 and DC-HF have been implemented into the GAMESS-US program. In this study, we present recent developments of the computational techniques for the rapid DC-MP2 calculations using massively parallel computers.

II. Two-level hierarchical parallelization scheme for DC-MP2 calculations [3]

We developed a two-level hierarchical parallelization scheme for the DC-MP2 calculations that is suitable for massively parallel computing. The parallelization scheme is a combination of the coarse-grain parallelization assigning each subsystem to a group of processors and the fine-grain parallelization where the computational tasks for evaluating the MP2 correlation energy of the assigned subsystem are distributed among processors in the group. Test calculations demonstrate the high parallel efficiency of the present two-level hierarchical parallel implementation, making the DC-MP2 calculations feasible for extended systems using massively parallel computers.

III. Semi-direct DC-MP2 method [3] and DC-RI-MP2 method

We developed a parallel semi-direct DC-MP2 code for the rapid calculations using the commodity PC clusters. This code is based on the semi-direct algorithm, in which third-quarter transformed integrals are stored on disks to avoid redundant multiple evaluation of electron repulsion integrals (ERIs). Furthermore, we developed a DC-RI-MP2 method by utilizing the resolution of identity (RI) approximation of ERIs to reduce the computational prefactor for the integral transformations and the disk and memory requirements. Test calculations demonstrate that these new implementations considerably speed up the DC-MP2 calculations of large molecules.

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4PP-23

Calculation of Rate Constant for Excitation Energy Transfer by Fermi's Golden Rule

Takuma Yamamoto, Satoshi Yabushita
Department of Chemistry, Faculty of Science & Technology, Keio University, Japan

We have tried to calculate the rate constant for excitation energy transfer (EET) within the Light-Harvesting complex (LH2) in photosynthetic Purple Bacteria. This rate constant cannot be estimated within the framework of the well-known Förster's formula because of the very small overlap between the luminescence spectrum of B800 and the absorption spectrum of B850. Instead, the rapid EET rate could be estimated by the first-order perturbation theory, namely Fermi's Golden rule.

If a total system Hamiltonian H is time independent, $\rho_I(t)$, the population of an initial state I is obtained from the formal solution of the Liouville equation as follows,

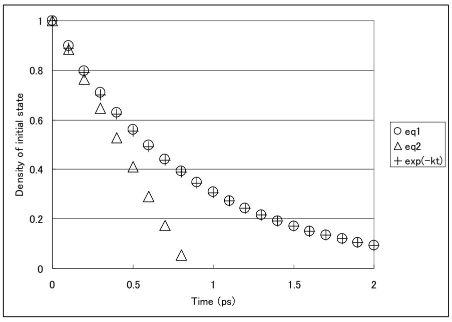
$$\rho_I(t) \equiv \sum_{i\in I}\langle i|\rho(t)|i\rangle = 1-4\sum_{i_1,i_2\in I,\alpha>\beta}\rho_{i_1}(0)U_{i_1\alpha}U_{i_2\alpha}U_{i_1\beta}U_{i_2\beta}\sin^2[\frac{(D_\alpha-D_\beta)t}{2\hbar}]. \qquad (1)$$

Here, U and D represent eigenvectors and eigenvalues of H, and the subscripts i_1, i_2 and α, β represent vibronic basis and vibronic eigenstates of H, respectively. By dividing H into nonperturbative part H_0 and pertubative part V ($H = H_0 + V$), we have

$$\rho_I(t) \approx 1-kt. \qquad k \equiv \frac{2\pi\rho}{\hbar}\left[\sum_{i\in I}\rho_i(0)V_i^2\right] \qquad (2)$$

Here, ρ represents the density of final vibronic states.

The magnitude of the pseudo-coulomb interaction V between B800 and B850 was estimated about 20 cm^{-1} by an interaction model using their transition dipole moments. Franck-Condon (FC) factor of B800, treated as a monomer, was estimated about 0.58 (HF/3-21G* for the ground state, CIS/3-21G* for the excited state), and V was set to be 6.7 ($=20\times0.58^2$) cm^{-1}. The decay feature of $\rho_I(t)$ calculated with Eqs. 1 and 2 are compared in Figure, and a rate constant of 0.85ps was derived.



This result is in agreement with experiment[1] in view of order. It suggests that we could estimate the rate constant in LH2 by Fermi's Golden rule if we obtain accurate information concerning vibration states and FC factors.

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4PP-24

Divide-and-conquer symmetry-adapted cluster method

Takeshi Yoshikawa,[1] Masato Kobayashi,[1,2] Hiromi Nakai[1,3,4]
[1] *School of Advanced Science and Engineering, Waseda University, Japan*
[2] *Institute for Molecular Science, Japan*
[3] *Research Institute for Science and Engineering, Waseda University, Japan*
[4] *CREST, Japan Science and Technology Agency, Japan*

I. Introduction

We have implemented and assessed the divide-and-conquer (DC) self-consistent field (SCF) method and extended the DC method to the post-HF correlation theories [1]. In this presentation, we will report the extension of the DC method to the symmetry-adapted cluster (SAC) theory [2] and show some illustrative applications.

II. Theory

In the DC-SAC method, the total correlation energy is estimated by summing up correlation energies corresponding to individual subsystems. The correlation energy of a subsystem is estimated using subsystem MOs, composed of the AOs of the non-overlapping central region and the environmental buffer region.

The SAC method introduces the perturbative configuration selection for reducing computational time. Namely, the double excitation operators ($\hat{S}_D$) whose second-order contribution to the energy E_D, given in Eq. (1), is greater than a given threshold (λ_g = 10^{-5} for level 1, 10^{-6} for level 3) are only included in the cluster expansion.

$$E_D = \frac{|H_{0D}|^2}{H_{DD} - H_{00}}, \quad H_{ab} = \left\langle \Phi_a \middle| H \middle| \Phi_b \right\rangle \tag{1}$$

III. Results

The present DC-SAC method was assessed in calculations of a hydrogen fluoride oligomer $(FH)_6$. In the DC calculations, one FH unit was adopted as a central region and several adjacent FH units were treated as the corresponding buffer region. Figure 1 shows buffer size (n_b) dependence of the correlation energies obtained by the DC-SAC and DC-CCSD calculations. While the CCSD energy difference between DC and conventional calculation for $n_b = 1$ is less than 1.5 mhartree, the SAC energy difference ($n_b = 1$) is 78.2 mhartree at level 3. On the other hand, the DC-SAC data ($n_b = 1$) at level 3 is close to that of the conventional without selection (green line) as well as the DC-SAC data ($n_b = 1$) without selection. This means that the perturbation selection with the small buffer efficiently describes the correlation effect, which is the similar effect as reported for SAC calculations with the localized orbitals [3].

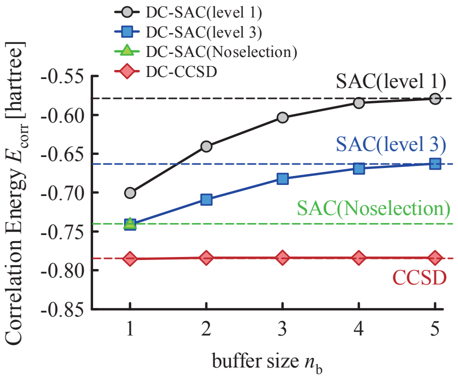

Fig. 1. Buffer-size dependence of DC-SAC and CCSD correlation energies of $(FH)_6$.

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4PP-25

Fast Diffusion of Water Confined Between Plane Surfaces Coated with Water Monolayer

Lukman Hakim,[1] Masakazu Matsumoto,[1] Hideki Tanaka[1]
[1]*Graduate school of Natural Science and Technology, Okayama University, Japan*

I. Introduction

The structure of water at interfaces can influence the physical and chemical process in biological and human-made systems. Water molecules can be chemically bound on the surface of certain material such as Pt to give a thin film of immobilized water [1]. Considering the variety of surface materials that can be prepared, it is plausible to obtain a particular arrangement of water molecules that exhibit property of interest. For example, water monolayer on the surface of Pt and Pd was reported to be hydrophobic on which water diffusion is facile [2]. Here we show that a simple model of water monolayer can give hydrophilic or hydrophobic-like property by varying its intermolecular distance, and further can accelerate the lateral diffusion of water confined between two plane surfaces coated with water monolayer.

II. Simulations

The water monolayer is modeled with the (111) surface of cubic ice having diamond-like structure. The system consists of two planes of wall, which are separated by 5 nm distance. The water monolayer is then immobilized on the wall surface and massive water molecules are confined between those walls. The structure and dynamics of water in liquid phase and in monolayer is investigated using molecular dynamics simulation at constant overall density of 1 g cm^{-3} and temperature of 298 K.

III. Results

The water monolayer of interest is exhibiting strong hydrophilic properties when the intermolecular distance is equal to those of cubic ice, followed by the low diffusion rate of water in adjacent layer. When the immobilized water molecule is brought to closer distance, the monolayer shows a hydrophobic-like properties where the hydrogen bond with the adjacent layer is not well formed, and consequently having higher diffusion rate which extends to the remaining water molecules.

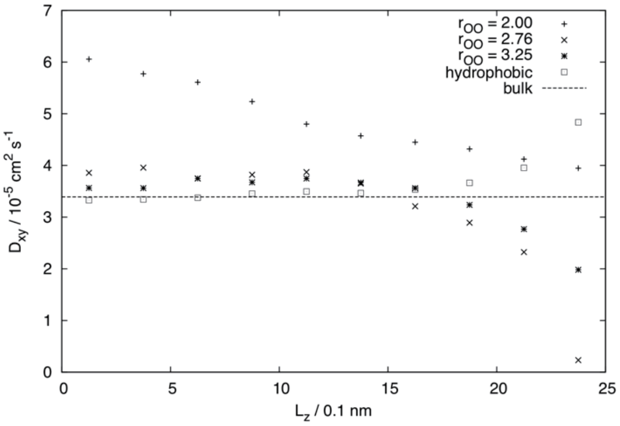

Fig 1. Lateral diffusion constant of the confined water. The water monolayer is located at L_z = 2.5 nm from the center of cell.

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4PP-26

On the Thermodynamic Stability of Hydrogen Hydrates of ice I_c and ice II structures: a theoretical and simulation study

Lukman Hakim,[1] Kenichiro Koga,[1] Hideki Tanaka[1]
[1] *Graduate school of Natural Science and Technology, Okayama University, Japan*

I. Introduction

Demand for a clean and renewable energy source leads to a wide investigation on alternative fuel materials. The simplest element for this purpose is perhaps hydrogen, which exhausts only water vapor when burnt. But the question on how to storage this gas for practical purpose is a challenge that drives engineers and scientists to consider hydrate compounds as an alternative. For that purpose, detail knowledge on the thermodynamic properties of hydrogen hydrate is required. Here we describe a theoretical-calculation and a Monte Carlo (MC) simulation that are both useful to access the thermodynamic properties of hydrogen hydrate of ice I_c and ice II structures [1].

II. Simulations and theoretical calculations

A hybrid type of MC simulations in grand-canonical ensemble is carried out to investigate the occupancy of hydrogen gas inside ice I_c and ice II, and the stability of both hydrates. The MC step consists of a trial of insertion-or-deletion of hydrogen gas inside the hydrate, a trial of displacement of hydrogen or water molecules, and a trial to change the system volume at constant pressure. The stability is quantified in term of chemical potentials through a theoretical calculation based on modified van der Waals Platteeuw theory [2]. An analysis for a relevant thermodynamic potential is done to derive the isothermal compressibility of both hydrates.

III. Results

The MC simulations provide a detail on hydrate structures and hydrogen gas occupancy at various thermodynamic states. The simulations also show the instability of ice I_c under partial occupancy of hydrogen gas, which lead to the formation of amorphous ice at high pressure. The gradual increase of hydrogen gas occupancy inside ice II during compression gives an anomalous compressibility curve. The phase boundaries can be established from the equilibrium state of one, two, and three-phases between pure ices, filled ices, and hydrogen fluid, from which a global phase diagram in pressure, temperature, and chemical composition spaces is constructed.

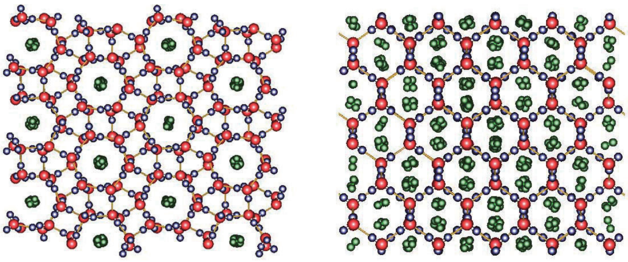


Fig 1. The structure of hydrogen hydrate of ice II (left) and ice I_c (right) structure from simulation.

[1] L. Hakim, K. Koga, H. Tanaka, Phys. Rev. Lett. 104, 11 (2010)
[2] H. Tanaka, T. Kiyohara, J. Chem. Phys. 98, 4098 (1993)

4PP-28

Description of time evolution and dielectric response based on Rigged QED

Masato Senami,[1] Akitomo Tachibana,[1]
[1]*Department of Micro Engineering, Kyoto University, Japan*

It is presented that a calculation code of time evolution of a system based on the Rigged QED theory [1,2]. QED has been proven as a very successful theory due to e.g. the prediction of the magnetic dipole moment of muon and scattering processes of free particles. However, its success is restricted if the assumption of free particle as an asymptotic field is good. Theories describing bound states, such as Bethe-Salpeter equation and NRQED [3], are still insufficient ones for us. Hence, we consider a method based on quantum theory of fields in this work, i.e. electrons, nucleus, and photons in bound states are described with creation/annihilation operators.

Matter fields are given as Schroedinger fields in our code. These are expanded as $\hat{\Psi}(t,\vec{x}) = \sum_p \hat{e}_p(t)\psi_p(E_p,\vec{x})$, where $\hat{e}_p(t)$ is an annihilation operator. We use the solution of the Schroedinger equation as the basis function, ψ. The time evolution of a field is given by,

$$i\frac{d}{dt}\hat{\Psi} = \hat{H}\hat{\Psi},\ \hat{H} = \frac{1}{2}\left(-i\vec{\nabla} - \frac{Z_e}{c}\hat{\vec{A}}\right)^2 + \frac{Z_e}{c}\hat{A}_0.$$

The photon field $\vec{A}$ contains both real photon particles $\hat{\vec{A}}_{\rm rad}$ and interaction fields $\hat{\vec{A}}_A$, i.e. virtual photons. These effects in field theory are much different from quantum mechanics. Particularly, the effect that long wavelength photons take energy away from a system can correctly be described in our method.

The time evolution of the operator is given by,

$$i\frac{d}{dt}\hat{e}_p(t) = \sum_q \int d^3\vec{x}\psi_p^\dagger(E_p,\vec{x})\left[\frac{1}{2}\left(-i\vec{\nabla} - \frac{Z_e}{c}\hat{\vec{A}}\right)^2 + \frac{Z_e}{c}\hat{A}_0\right]\psi_q(E_q,\vec{x})\hat{e}_q(t).$$

Actually, pursuing the evolution is very hard task. One reason is that after some steps the operator is very high order polynomial of some operators, and hence algebraic computation using commutation relation are very hard. Moreover, the problem of the divergence from loop diagrams is not so simple for the dynamics of bound states, since ordinary renormalization is formulated for an asymptotic free field. Hence, we should take special care of a prescription of renormalization. In this work, we present the polarization response of a system by injection photon by using our calculation code.

[1] A. Tachibana, J. Mol. Modelling **11**, 301 (2005).
[2] A. Tachibana, J. Mol. Struct. (THEOCHEM), **943**, 138 (2010).
[3] W. E. Caswell and G. P. Lepage, Phys. Lett. **167B**, 437 (1986).

4PP-29

A comparative *ab initio* multireference Møller-Plesset perturbation study for N_2O binding and activation by atomic excited states of Au, Pd, Pt and Rh

Oscar Olvera-Neria,[1] Virineya Bertin,[2] Víctor Hugo Uc-Rosas,[1] Alberto Rubio-Ponce,[1] and Enrique Poulain[1]
[1]*Área de Física Atómica Molecular Aplicada (FAMA), CBI, Universidad Autónoma Metropolitana-Azcapotzalco, México*
[2]*Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa,México*

I. Introduction

Nitrous oxide (N_2O) is an intermediate compound formed during catalysis occurring in automobile exhaust pipes. Therefore, it is important to propose some mechanisms to reduce N_2O to N_2 employing platinum group metals (PGMs) as catalysts.

Calculations were performed using the multireference plus second-order perturbation theory (MRPT2) level of theory, the *ab initio* method of choice for this kind of work. The study consider the interaction of N_2O with a single Pd, Pt, Rh and Au atoms, respectively, in ground and excited states, as well as their corresponding cations, with the aim of achieving a satisfactory interpretation of the catalytic reaction mechanism for the formation of the corresponding adducts and the dissociation of N_2O.

II. Results

We found that ground state of Rh and Au atoms are not able to capture nitrous oxide. Reactions 1-6 show that the excited states of Rh, Pt and Au atoms are active in the capture and dissociation of N_2O, according to the reactions for the active atomic lowest energy state:

$$RhN_2O\ (^6A') \rightarrow RhO\ (^6A') + N_2\ (^1\Sigma g^+) \tag{1}$$
$$Au\ (^4A') + N_2O\ (^1\Sigma^+) \rightarrow AuO\ (^4A') + N_2\ (^1\Sigma g^+) \tag{2}$$
$$Au^+\ (^5A') + N_2O\ (^1\Sigma^+) \rightarrow NAuNO^+\ (^5A') \tag{3}$$
$$Pt\ (^5A') + N_2O\ (^1\Sigma^+) \rightarrow PtO\ (^5A') + N_2\ (^1\Sigma g^+) \tag{4}$$
$$Pt^+\ (^6A') + N_2O\ (^1\Sigma^+) \rightarrow Pt^+\ (^4A') + N_2\ (^1\Sigma g^+) + O\ (^3P_2) \tag{5}$$

Pd atom does not activate the nitrous oxide, even in excited state. Although Pt and Au atoms reduce N_2O to N_2, the Rh atom requires less energy to carry out the transformation, because their ground and active lowest excited state are overlapped. On the three-way catalytic converters, Rh is used for reduction reactions and Pt and Pd in the oxidation reactions, as is also shown in these calculations. Rh, Pt and Au excited states role on the N_2O activation is to promote the charge transfer from transition metal to N_2O, this process does not occur with Pd as catalyst.

[1] William B. Tolman, Angew. Chem. Int. Ed. 49 (6), 1018-1024 (2010).

4PP-30

First principle calculation for hydriding reaction of metal boride

Y. Kawamura[1], T. Matsunaga[1], Y. Takeda[1], K. Miwa[2]
[1]*Toyota Motor Corporation, Japan*
[2]*Toyota central R&D laboratory, Japan*

I. Introduction

Boron hydride complexes, such as $LiBH_4$, $Mg(BH_4)_2$, are expected as the hydrogen storage materials because of its high gravimetric hydrogen density. The hydriding reaction from boron, $2B + 2LiH + 3H_2 \rightarrow 2LiBH_4$, requires very high temperature and high pressure of hydrogen (873K, 35MPa H_2) [1]. In contrast, the reaction from metal boride, such as MgB_2, proceeds under comparatively low temperature and pressure [2].

$$MgB_2 + 2LiH + 4H_2 \rightarrow 2LiBH_4 + MgH_2 \quad @\ 588K,\ 0.5MPa\ H_2 \quad (1)$$

In order to clarify the mechanism of these reactions, density functional calculation was performed and the difference of the reactivity was examined.

II. Method

In this work, the intermediates of the initial steps of hydriding reactions were examined. Energy differences (ΔE) between the reactant (B, MgB_2) and the intermediate were evaluated as a descriptor of reactivity. All calculations were performed within the GGA framework by using PBE functional. The planewave basis and ultrasoft pseudopotential were used as implemented in CASTEP program package.

Table 1. Energy difference ΔE between reactant and intermediate [kJ/mol H_2]

intermediate	B	MgB2	AlB2
H solvation	459	109	203
B defect	326	162	215
B defect + H2	246	104	202
Metal defect	--	172	59
M defect + H2	--	73	144

III. Results and discussion

The calculated ΔE values of MgB_2 were small compared to boron (Table 1). In particular, hydrogen addition to boron in MgB_2 produces relatively stable intermediates, which implies small reaction barriers of the hydriding steps for reaction (1). Ion doping effect was also investigated and the result shows that Li doping decreases ΔE value (Fig. 1). The Li(or Al)-doped MgB_2 were synthesized by the heat treatment to the mixture of Mg, B, and LiH(or Al). Absorbed H_2 amount of Li-doped MgB_2 was successfully improved, as expected by the calculated intermediate stability (Fig. 1).

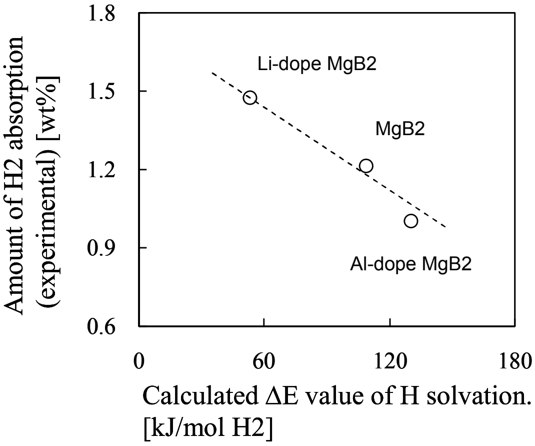


Fig. 1. Correlation between calculated ΔE values and experimentally measured H_2 amount of absorption.

[1] S. Orimo, et al, J. Alloys and Comp., 404 (2005) 427.

[2] J. Barkhordarian, et al, J. Alloys and Comp., 440 (2007) L18.

4PP-31

“Paired interacting orbitals(PIO)” analysis of phenoxyimine-based olefin polymerization catalysts

Akinobu Shiga,[1,2] Zygmunt Flisak,[3]
[1]*Frontier Research Center, Tokyo Institute of Technology, Japan*
[2]*LUMMOX Research Lab., Japan*
[3]*Faculty of Chemistry, University of Opole, Poland*

I. Introduction

Polyolefin is one of the most useful plastics for modern human life. Saving energy and resources, which is the most important issue of polyolefin production, is attained by using high mileage polymerization catalysts, e.g. phenoxyimine-based (FI) systems that belong to the post metallocene gloup. Here we clarify the role of phenoxyimine ligand by using PIO analysis, proposed by Fujimoto et al [1a].

II. Models and calculation methods

We employed the TS of ethylene insertion of four isomeric FI-methyl-Ti/ethylene systems: (a) N,Ncis-O,Otrans ethylene(E) trans to N, (b) N,Ntrans-O,Ocis E to O, (c) N,Ncis-O,Ocis_E to N, (d) N,Ncis-O,Ocis_E to O [2].

We divided the TS structures into two parts: fragment [A]:catalyst with the counter anion, and fragment [B]:ethylene, as shown in Figure 1. PIO calculation was carried out on the LUMMOX^{TM} system[1b]

III. Results and discussion

Overlap populations (OP) of PIO-1 and PIO-2 and ΣOP of each TS are summarized in Table 1. The larger the OP, the larger the reactivity toward the insertion. We can estimate that the reactivity decreases in the following order: (c) > (a) > (d) > (b). This order coincides with the order of insertion barriers obtained by DFT calculations with the exception of (c). The reason why is presented in the poster.

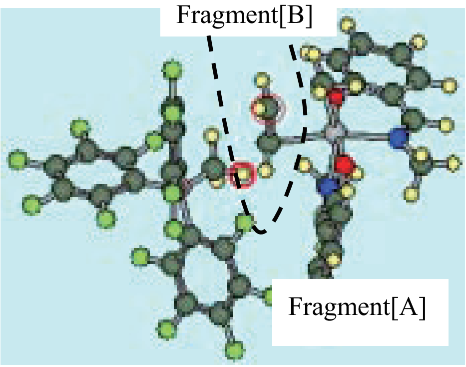


Figure 1 The fragmentation of TS

Table 1 Overlap Populations(OP) of PIO-1 and PIO-2 and ΣOP of each TS.

Model	ethylene	PIO-1	PIO-2	ΣOP	Insertion barriers(kcal/mol)[2]
(a) N,Ncis-O,Otrans	trans to N	0.1743	0.2050	0.3793	6.9
(b) N,Ntrans-O,Ocis	trans to O	0.1673	0.1708	0.3381	19.4
(c) N,Ncis-O,Ocis	trans to N	0.2117	0.2324	0.4441	17.1
(d) N,Ncis-O,Ocis	trans to O	0.1833	0.1796	0.3629	11.0

[1] a) H.Fujimoto, Acc. *Chem. Res.,* **20** 448 (1987). b) T. Motoki, A. Shiga, *J. Computational Chem.,* **25** 106 (2004). [2] Z. Flisak, P. Suchorska, Organometallics, **29** 6196 (2010)

4PP-32

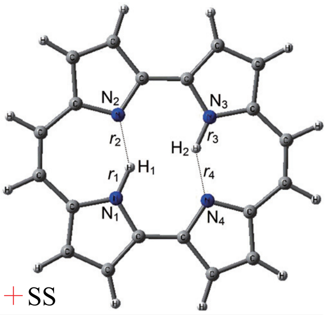
Quantum tautomerization in porphycene and its istopomers: Path-integral molecular dynamics simulations

T. Yoshikawa,[1] S. Sugawara, [1] T. Takayanagi, [1] M. Shiga,[2] M. Tachikawa[3]
[1] *Department of Chemistry, Saitama University, Japan*
[2]*Japan Atomic Energy Agency, Japan*
[3]*Quantum Chemistry Division, Yokohama City University, Japan*

I. *Introduction*

Multiple proton transfer is one of the most fundamental chemical reactions and has been observed in a wide range of molecular systems. A basic question to be solved is whether the transfer occurs via a concerted or stepwise mechanism. The question has been frequently addressed by using static electronic structure calculations of the potential energy surface. However, this simplified picture cannot be generally applied without considering the nuclear quantum effects, which is tunneling and zero-point harmonic energy.

In this work, path-integral molecular dynamics simulations (PIMD), that can give important information on nuclear quantum effects, have been performed for porphycene and its isotope variants in order to understand the double proton transfer mechanism of inner protons/deuterons from a quantum mechanical viewpoint [1–2]



II. *Calculation*

The PIMD simulations were carried out with 24 – 40 beads depending on the system temperature as well as isotopic substitution (HH, HD, DD). The time increment was set to Δt = 0.12 – 0.24 fs.

III. *Results and Discussion*

Fig. 1 displays the 2D contour plots of the inner proton/deuteron distributions obtained by the PIMD simulations at T = 300 K and 500 K. This result indicates that double proton transfer between *trans*–*trans* for HH at 300 K mainly occurs through the concerted mechanism and the contribution of the stepwise mechanism increases with an increases in temperature. We conclude that double proton transfer mechanism in porphycene depends on both temperature and isotopic substitution effects.

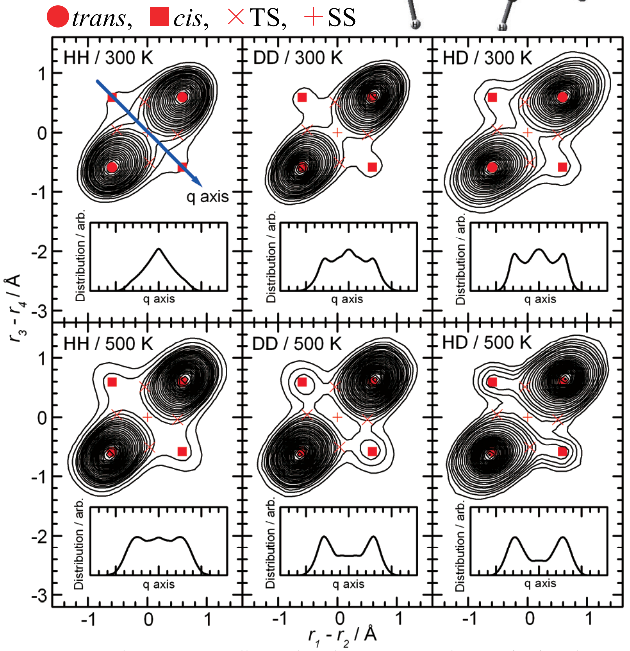


Fig. 1 Two-dimensional contour plots of the inner proton/deuteron distributions and its isotopic variants as a function of r_1–r_2 and r_3–r_4 coordinates obtained by the PIMD simulations at T = 300 K (top) and 500 K (bottom).

[1] Z. Smedarchina et. al., *Chem. Phys. Lett.* **436** (2007) 314-321.
[2] A. Vdovin, J. Waluk, B. Dick, A. Slenczka, *Chem. Phys. Chem.* **10** (2009) 761-765.

4PP-33

Acceleration of CASSCF–MD Simulation and its Application to Intramolecular Charge Transfer System

Masaki Okoshi[1] and Hiromi Nakai[1,2,3]
[1]*School of Advanced Science and Engineering, Waseda University, Japan*
[2]*Research Institute for Science and Engineering, Waseda University, Japan*
[3]*JST-CREST, Japan Science and Technology Agency, Japan*

Excited-states dynamics such as photo-induced chemical reactions and photo-induced charge transfers plays an important role in photo-functional materials. 4-(*N*,*N*-Dimethylamino)benzonitrile (DMABN; Figure 1) is one of the most investigated compounds, which causes an intramolecular charge transfer (ICT) along with geometric relaxations in the S_1 excited state. Although the electronic dynamics and the geometric changes have been extensively investigated experimentally and theoretically [1, 2], the mechanism of ICT remains under debate.

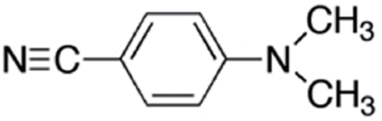


Figure 1. Structure of DMABN

The *ab initio* molecular dynamics (AIMD) simulation is one of the most suitable and promising methods, which enables microscopic modelings and direct observations of dynamical processes regarding chemical reactions. However, the system sizes and/or the simulation time are limited due to the extremely high computational cost of *ab initio* calculations. Thus, our group has proposed acceleration techniques named the Lagrange interpolation of molecular orbital (LIMO) method [3] and the least square of molecular orbital (LSMO) method [4], which enhance the convergence of self-consistent-field calculation at each AIMD step.

In the present study, the LIMO method is extended to CASSCF in order to perform efficient AIMD simulations for excited states. Using the accelerated AIMD simulations, the mechanism of ICT of DMABN accompanying the geometric relaxations is theoretically investigated.

The analyses confirm that ICT occurs with the elongation of the bond between the NMe_2 group and the benzene ring. The elongation of the bond hinders the coupling between the p orbital of the NMe_2 group and the π conjugated system of the benzonitrile group, and as a result, leads to the electron transfer from the NMe_2 to benzonitrile groups.

[1] J. Dreyer and A. Kummrow, *J. Am. Chem. Soc.* **122**, 2577 (2000).
[2] J.M. Rhinehart et al., *J. Phys. Chem. B* **114**, 14646 (2010).
[3] T. Atsumi and H. Nakai, *J. Chem. Phys.* **128**, 094101 (2008).
[4] T. Atsumi and H. Nakai, *Chem. Phys. Lett.* **490**, 102 (2010).

4PP-34

Theoretical study on the reaction mechanism of formation of 3,5-diacetyl-1,4-dihydrolutidine

Hiroyuki Teramae[1], Yasuko Y. Maruo[2], Jiro Nakamura [2]
[1] *Department of Chemistry, Josai University, Japan*
[2] *NTT Energy & Environmental Labs., Japan*

I. Introduction

The measurement of the formaldehyde is based on the acetyl acetone method (Nash Reagent) in the aqueous solution as shown in scheme Fig 1. The method utilizes the reaction of two acetyl acetone molecule, ammonium ion, and formaldehyde molecule yielding the lutidine derivative. Very recently, Maruo and co-workers [1] found that β diketones (pentane-2,4-dione (R_1,R_2 = CH_3) 1-phenyl-1,3-butanedione (R_1=CH_3, R_2=Ph) or 1,3-diphenyl-1-3-propanedione (R_1=Ph, R_2 =Ph)), and ammonium salts in porous glass can be used for a measurement of formaldehyde in the gas phase. As a first step of figuring out the behavior of the lutidine derivative in porous glass, we perform *ab initio* molecular orbital calculations to obtain the reaction path from pentane-2,4-dione to the lutidine derivative.

II. Method of Calculations

The HF/3-21G and MP2/6-31G** level molecular orbital calculations are performed on the lutidine derivative (3,5-diacetyl-1,4-dihydrolutidine, IUPAC name 3,5-diacetyl-1,4-dihydro-2,6- dimethylpyridine

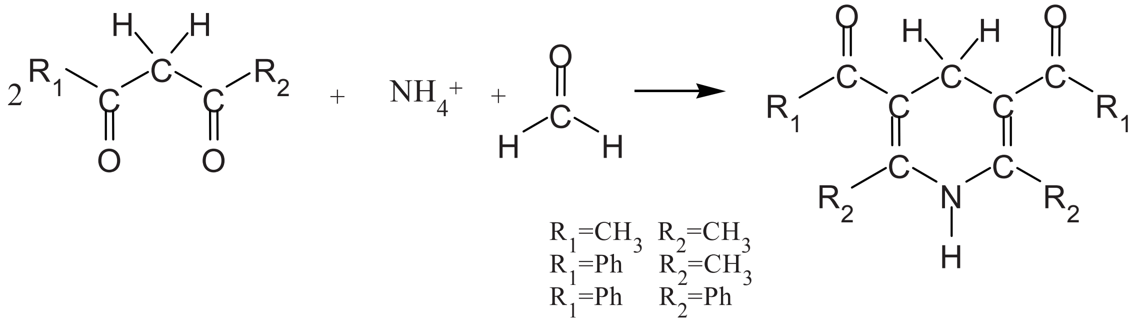


Figure 1. The reaction formula of the formation of the lutidine derivatives,

III. Results and discussion

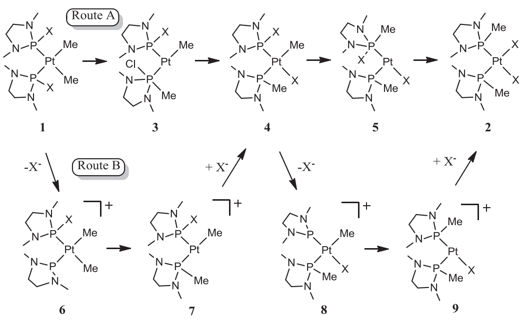
The first step of the reaction, for example, would be a formation of 4-amino-3-penten-2-one (FLUORAL-P) from 2,4-pentanedione and ammonia. The largest barrier height was found to be about 57 kcal/mol at HF/3-21G level, which is the H_2O elimination yielding FLUORAL-P. The barrier height is reduced to about 52 kcal/mol at the MP2/6-31G**. The energy is still high, however, will be further reduced by the solvation.

[1] Maruo, Y. Y.; Nakamura, J.; Uchiyama, M., *Talanta*, 74 (2008) 1141–1147.

4PP-35

DFT Study of Methyl/Halogen Exchange Reaction on Pt Complexes with Phosphine Ligand

Noriko Tsuchida,[1] Mari Takashima,[2] Yuka Shigesato,[3] Masumi Itazaki,[3] Hiroshi Nakazawa,[3] and Keiko Takano[2]
[1]*Ochadai Academic Production, Ochanomizu University, Japan*
[2]*Gradute School of Humanities and Sciences,Ochanomizu University, Japan*
[3]*Department of Chemistry, Graduate School of Science, Osaka City University, Japan*



Scheme 1 Two plausible reaction pathways

Phosphine ligands, PR_3, are inactive per se, but provide the central metal with specific electronic, steric, or chiral environment. In this context, structural change of the phosphine ligand in complexes would not be preferable. However, several reactions associated with structural change of the ligand are observed in phosphine complexes. The studies of these reactions have attracted considerable attention from the viewpoint of catalytic functions [1]. We recently found unprecedented Me/X (X = Cl, Br) exchange reaction for $PtMe_2\{PX(NCH_3CH_2)_2\}_2$ (**1**). Understanding the mechanistic feature of this reaction is crucial for development of phosphine complex catalysts. The exchange reaction pathway was examined using quantum chemical calculations.

Two reaction pathways, Routes A and B, are conceivable for the Me/X exchange reaction (Scheme 1) [1-3]. To examine which reaction pathway is more feasible, we conducted DFT calculations for **1**. All calculations were carried out using the B3PW91/SDD with PCM.

In Route A for the Me/X exchange involving metallaphosphoranes (**3** and **5**) as intermediates, stationary points were not found for metallaphosphoranes as stable intermediates. In contrast, complex **1** can be converted into **4** with small activation energy in Route B. The activation free energies of Me migration (from **6** to **7** and from **8** to **9**) for the Me/Br exchange reaction is 6.36 and 2.11 kcal/mol, respectively (Figure 1). Route B for Me/X (X = Cl, Br) is more preferable to Route A for the conversion of **1** into **2**.

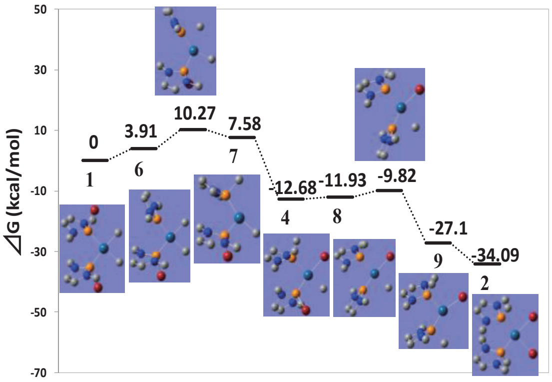


Figure 1. Energy diagram of Me/Br exchange reaction in Route B calculated by B3PW91/SDD with PCM.

[1] R. N. Perutz, et al., *Chem. Commun.*, 2749 (2002) [2] R. N. Perutz, et al., *J. Am. Chem. Soc.*, **130**, 15499 (2008) [3] S. A. Macgregor, et al., *J. Am. Chem. Soc.*, **130**, 15490 (2008)

4PP-36

FMO-MD simulations for hydrated trivalent lanthanide ions using 4f-in-core model core potentials

Takayuki Fujiwara[1], Yuji Mochizuki[1,2], Hirotoshi Mori[3], Yuto Komeiji[4],
Tatsuya Nakano[2,5], Yoshio Okiyama[2], Eisaku Miyoshi[6]
[1]*Rikkyo University, Tokyo, Japan,*
[2]*Institute of Industrial Science, Tokyo University, Tokyo, Japan.*
[3]*Division of Advanced Sciences, Ochanomizu University, Tokyo, Japan.*
[4]*National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.*
[5]*Division of Medicinal Safety Science, National Institute of Health Sciences, Tokyo, Japan.*
[6]*Graduate School of Engineering Sciences, Kyushu University, Fukuoka, Japan.*

I. Introduction

The hydration phenomena of metal ions have attracted considerable interests. In the field of inorganic chemistry, the lanthanide contraction as well as the gadolinium break have been well known. However, the number of theoretical studies on these is rather limited. In the present study, we perform the method of fragment molecular orbital-based molecular dynamics (FMO-MD [1]) simulations for the droplet models containing Ln^{3+} (Ln=La, Eu, Gd, Tb, Lu). The hydration structures are evaluated, and the charge distributions in hydration shells are analyzed in detail.

II. Computational procedure

We first prepared the large-core MCP basis sets in which the chemically inert 4f electrons in Ln^{3+} are treated through effective potentials (termed as 4f-in-core MCPs) [2]. The use of this MCP technique enabled the closed-shell calculations throughout, leading to the computational benefits. The MD simulations were done for $Ln(H_2O)_{64}{}^{3+}$ droplet model at the FMO3-HF level under the Nosé–Hoover chains method, and the statistical quantities were evaluated with a series of configurations during 1-3 ps at 300 K.

III. Results and discussion

As the representative indices of hydration structure, we here address the first peak positions of radial distribution functions (RDFs) of Ln^{3+}-O for the $Ln^{3+} = La^{3+}$ and Lu^{3+} cases. The respective values were predicted to be 2.59 Å and 2.31 Å, and the lanthanide contraction in our simulation was 0.28 Å. The theoretically predicted Ln^{3+}-O lengths were in good agreement with the EXAFS observations as 2.54 Å and 2.31 Å. The coordination numbers of Ln^{3+} were 9 for La^{3+} and 8 for Lu^{3+}. The difference in the hydration environments was clearly reflected in the different characteristics of the angular distribution functions (ADFs) of O-Ln-O as well as the natural populations, too. Detailed discussion including correlation effect will be presented at the poster session.

[1] Y. Komeiji *et al.*, *Chem. Phys. Lett.*, **484**, 380 (2010).

[2] T. Fujiwara *et al.*, *Chem. Phys. Lett.*, **510**, 261 (2011).

4PP-37

Quantum dynamics study of the MuFF reaction system

Tomokazu Tanaka,[1] Toshiyuki Takayanagi[1]
[1]*Department of Chemistry, Saitama University, Japan*

I. Introduction

Muonium (Mu) which is an ultralight isotope of hydrogen composed of a positive muon (μ^+) and an electron (e^-), since the mass of μ^+ is about 1/9 of the proton mass. Although the lifetime of Mu is quite short (~ 2.2 μs), this timescale is long enough for investigating chemical reactions from the experimental side. In particular, Mu has long been used to probe important quantum effects including tunneling and quantized vibrations in reaction dynamics fields and there have been many studies reporting anomalous isotope effects.

Quantum dynamics calculations for the $Mu + F_2 \rightarrow MuF + F$ and $F + MuF \rightarrow FMu + F$ reactions have been performed on a global potential energy surface developed at an *ab initio* multi-reference configuration interaction electronic structure level. Although thermal rate constants for the $Mu + F_2$ reaction were calculated to be slightly smaller than experimental measurements, the strongly curved behavior observed in the Arrhenius plot of the measured data has been reproduced by the present quantum dynamics calculations.

In the case of $F + MuF \rightarrow FMu + F$ exchange reaction, we have observed very large resonance peaks around the asymptotic F + MuF(v,j) energy level(Figure 1). Detailed analyses show that the observed resonances are associated with the quasi-bound states localized around the F···MuF potential well having a strong hydrogen bonded character. We found that those states can significantly contribute to the reaction probabilities above the reaction threshold energy.

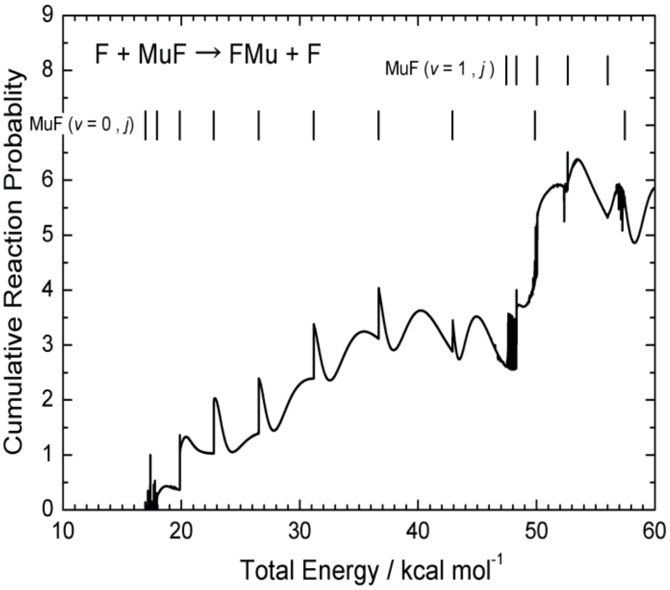


Figure 1
Cumulative reaction probabilities for the $F + MuF \rightarrow FMu + F$ exchange reactions as a function of the total energy, which is measured from the F + MuF asymptotic potential bottom. The asymptotic energy levels for F + MuF(v,j) are also shown, where v and j are vibrational and rotational quantum numbers, respectively.

4PP-38

Quantum proton transfer in hydrated sulfuric acid clusters

S. Sugawara,[1] T. Yoshikawa,[1] T. Takayanagi,[1] M. Shiga,[2] M. Tachikawa[3]
[1] *Department of Chemistry, Saitama University, Japan*
[2]*Japan Atomic Energy Agency, Japan*
[3]*Quantum Chemistry Division, Yokohama City University, Japan*

H_2SO_4 is a strong acid and is known to show acid dissociation into H^+ and HSO_4^- or SO_4^{2-} in water. The fundamental aspect is to find out how many water molecules are needed for acid dissociation of the H_2SO_4 molecule in water environment. In order to address this issue, electronic structure calculations have been so far performed for the $H_2SO_4(H_2O)_n$ cluster systems[1]. The previous studies found that sulfuric acid can be dissociated into HSO_4^- in clusters containing four water molecules and be fully dissociated into SO_4^{2-} in clusters containing eight or more water molecules. More recently, theoretical studies have focused on dynamical aspects of the hydrated sulfuric acid system using first-principles molecular dynamics approach[2].

We are interested in nuclear quantum effects on the proton transfer. Path-integral molecular dynamics (PIMD) simulation is a useful method for understanding the effects of both quantum nature and thermal fluctuation of nuclei. To understand acid dissociation mechanisms from quantum viewpoint, we performed PIMD simulations for the $H_2SO_4(H_2O)_n$ (n = 4–12) clusters at 300 K.

Figure 1 shows the two-dimensional contour plots of the probability distribution obtained from the PIMD simulation for n = 4 as a function of ΔR and the collective coordinate C_w. C_w is a dimensionless coordination number of water with respect to the proton-accepting water. From the result in Figure 1, it is seen that the proton-transfer process is strongly correlated with C_w; the ionic dissociation to form HSO_4^- effectively occurs when the water coordination number C_w becomes large.

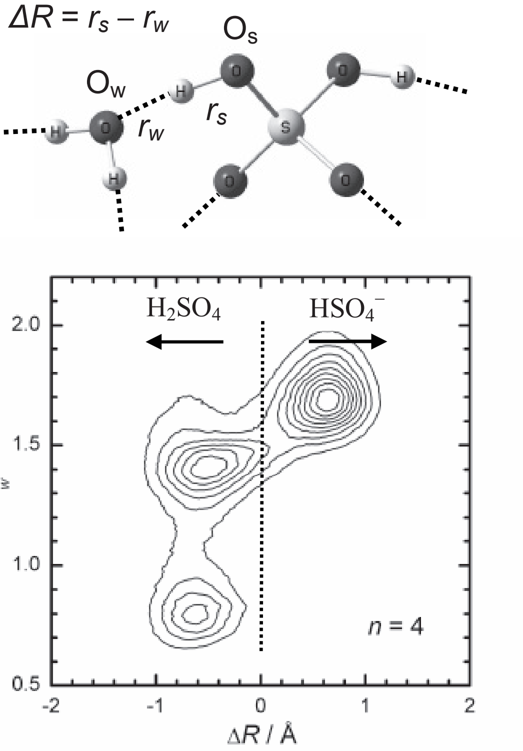


Figure 1. Two-dimensional contour plots of $H_2SO_4(H_2O)_4$ cluster as a function of ΔR and C_w.

[1]S. Re, Y. Osamura, K. Morokuma, *J. Phys. Chem. A* **103** (1999) 3535-3547.

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4PP-39

Noble Features in Oxidative Addition of B−Br σ−Bond of Bromoborane to $M(PMe_3)_2$ (M= Pt or Pd): Theoretical Study

Guixiang Zeng[1], Shigeyoshi Sakaki*[1]
[1]Fukui Institute for Fundamental Chemistry, Kyoto University

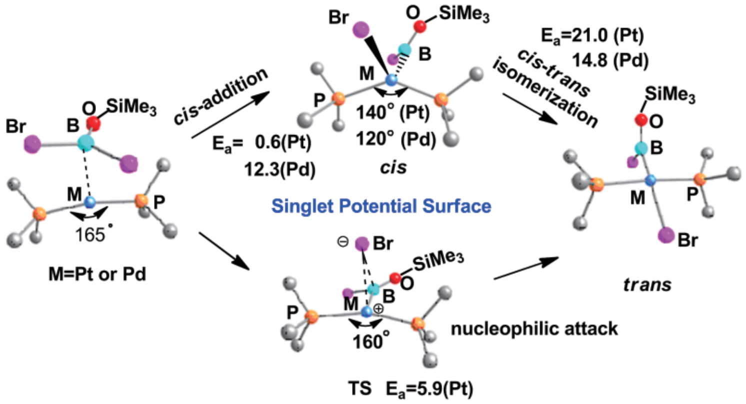
I. Introduction

Formation processes of *cis*−boryl complex via oxidative additions of B−H, B−B, and B−E (E=Si, Ge, or Sn) bonds to low−valent transition−metal complexes have been clarified theoretically.[1] However, the mechanism for *trans*-boryl complex produced by the oxidative addition of B−X (X=Cl, Br, or I) bond to Pd(0) and Pt(0) complexes remains unclear yet, in which the cis−trans isomerization is proposed to be involved. However, the cis-trans isomerization occurs via spin conversion process in general, [2] but the cis-trans isomerization taking place on single potential surface has not been investigated well. Here, we theoretically investigated the oxidative addition of the B−Br bond of bromoborane $Br_2B(OSiMe_3)$ to $M(PMe_3)_2$ (M = Pt or Pd) to explore possible reaction pathways and to clarify the process of the thermal cis−trans isomerization in this reaction.[3]

II. Computational Details

Geometry and frequency calculations were carried out by DFT method with triple-zeta quality basis sets. The singlet−triplet energy difference was evaluated with DFT and MP2 to MP4(SDQ) methods.

III. Results and Discussion



Scheme 1

E_a (kcal/mol) is Gibbs energy barrier in solvent (toluene).

The first step is the coordination of $Br_2B(OSiMe_3)$ with $M(PMe_3)_2$ (M = Pt or Pd) to form a precursor complex. The next is the B−Br bond cleavage. In the Pt system, two reaction courses are possible (Scheme 1); one is the nucleophilic attack pathway which directly affords the *trans*-product. The other one is the stepwise reaction pathway which includes the *cis*−oxidative addition followed by the cis−trans isomerization. The former reaction course is more favorable. In the Pd system, only the stepwise pathway was found. Interestingly, the thermal cis−trans isomerization was found to occur on the singlet potential energy surface due to the strong donation ability of the boryl group.

[1] Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179. [2] Gaspar, A. B.; Ksenofontov, V.; Seredyuk, M.; Gütlich, P. Coord. *Chem. Rev.* **2005**, *249*, 2661. [3] Zeng, G.; Sakaki, S. *Inorg. Chem.* **2011**, *50*, 5290.

4PP-40

Theoretical study on aquation reaction of *cis*-platin complex using RISM-SCF-SEDD.

Daisuke Yokogawa,[1] Kohei Ono,[2] Hirofumi Sato[2], and Shigeyoshi Sakaki[3]
[1]*Institute for Protein Research, Osaka University, Japan*
[2]*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Japan*
[3]*Institute for Integrated Cell-Material Sciences, Kyoto University, Japan*

The *cis*-diamminedichloro-platinum (II) (*cis*-platin) is a well-known anti-cancer drug established in 1970's and still being used. In the human body, injected *cis*-platin (**1**) is hydrolyzed to lose a chloride anion.

$$\mathrm{Pt(NH_3)_2Cl_2 + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-}$$

The monoaqua complex (**2**) reacts with another water to afford diaqua complex (**3**),

$$\mathrm{[Pt(NH_3)_2Cl(H_2O)]^+ + H_2O \rightarrow [Pt(NH_3)_2(H_2O)_2]^{2+} + Cl^-}\ .$$

We investigated the reactions using RISM-SCF-SEDD, which is a hybrid approach of quantum chemical method and statistical mechanics. The geometries were computed using DFT/B3LYP in gas phase. The energies in gas phase and aqueous phase were evaluated with CCSD(T).

In Fig. 1, free energy changes of the reaction in the gas phase and in aqueous phase are shown. The first dissociation step of chloride anion in gas phase requires large amounts of energy (108.2kcal/mol) to overcome the strong electrostatic interaction between Pt complex and chloride anion. The dissociation of another chloride anion in complex **2** requires 195.7 kcal/mol. In aqueous phase, on the other hand, the dissociation steps are greatly stabilized by solvent waters. This is because the strong attractive interaction between two charged species is screened by solvent waters. The free energy in aqueous phase indicates that the aquation reaction occurs under a mild condition in water.

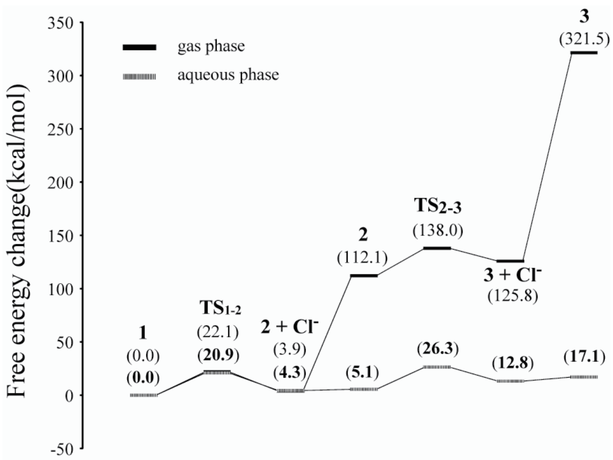


Figure 1. Free energy changes of the reaction in the gas phase, and in aqueous phase.

4PP-41

Theoretical Study of the Mechanism of the Excited-state Double Proton Transfer in 7-azaindole Dimer

Xue-fang Yu, Shohei Yamazaki, and Tetsuya Taketsugu
Department of Chemistry, Graduate School of Science, Hokkaido University, Japan

The excited-state double proton transfer (ESDPT) in 7-azaindole dimer is theoretically investigated by means of high-level electronic-structure calculations. The long-range corrected (LC) TDDFT [1] method and CASPT2 method are employed for geometry optimizations as well as single-point energy calculations of the excited-state potential energy profiles along the reaction paths. The resulting potential energy curves suggest that the ESDPT in the gas phase can proceed in the lowest locally-excited state through single transition state and without any intermediate for single proton transferred component [2]. It is therefore likely that the ESDPT in locally-excited state follows the concerted mechanism [3-4]. The concerted ESDPT is found to occur asynchronously in C_s symmetry rather than synchronously in C_{2h} symmetry. The step-wise mechanism [5] of ESDPT via the charge transfer state is also examined using LC-TDDFT method.

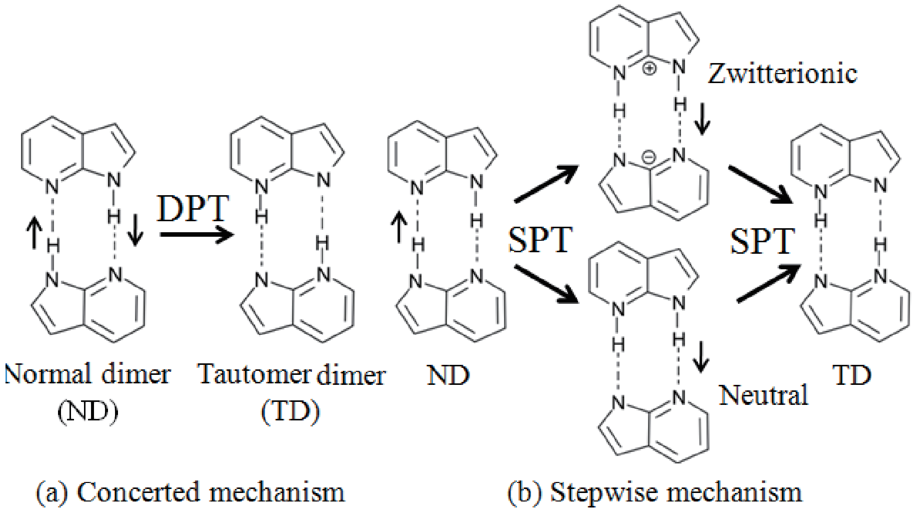


Figure 1. Concerted mechanism and step-wise mechanism of ESDPT in 7AI-dimer.

[1] M. Chiba, T. Tsuneda and K. Hirao, J. Chem. Phys., 124, 144106 (2006).
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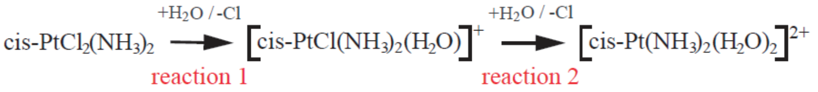
4PP-42

Solvation Effect on Hydrolysis of cis- and trans-Platins

Shinji Aono,[1] Shigeyoshi Sakaki[1*]
[1]*Fukui Institute for Fundamental Chemistry, Kyoto University, Japan*

I. Introduction: Cis-platin (cis-$PtCl_2(NH_3)_2$) is well-known as an anti-tumor drug and its derivatives have been extensively investigated in both experimental and theoretical fields. Before cis-platin interacts with the cellular DNA, hydrolysis of cis-platin occurs as one of key steps (Scheme 1). The substitution of Cl^- for H_2O changes the net charge of the Pt complex, indicating that the equilibrium solvation structure significantly changes. To understand the hydrolysis correctly, we need the clear insight into solvation. Here we investigated the hydrolysis of cis- and trans-platins with the 3D-RISM-SCF method.



$$\text{cis-}PtCl_2(NH_3)_2 \xrightarrow[\text{reaction 1}]{+H_2O\,/\,-Cl} \left[\text{cis-}PtCl(NH_3)_2(H_2O)\right]^{+} \xrightarrow[\text{reaction 2}]{+H_2O\,/\,-Cl} \left[\text{cis-}Pt(NH_3)_2(H_2O)_2\right]^{2+}$$

Scheme 1 : Hydrolysis of cis-platin

II. Computational Detail: The geometry optimization was carried out by the DFT method with M06-2X functional. To evaluate the free energy, the MP2 calculation was performed by using the 3D-RISM-RHF wavefunction as the zeroth order state. The LANL2TZ(f) basis sets were used for Pt atom by replacing its 60 core electrons with the Hay-Wadt ECP. The cc-pVTZ basis sets were used for all ligands and augmented functions were added to O and Cl. To make the thermo-dynamical correction of solute motion, the zero point energy, thermal energy, and entropy contribution were added [1].

III. Result: We consider the reactant dissociated state (RS) and associated state (RAS) and product dissociative and associative states (PS and PAS); see Fig.1. In solution, the RS and RAS conceptually represent the same initial state, except for the different position of one water treated quantum-mechanically. The small free energy difference between the RS and RAS (Fig.1) indicates that the 3D-RISM-SCF method gives the reasonable description of hydrogen bonds near the Pt complex in a statistical classical manner. Taking RAS as the initial state, the activation and reaction free energies are calculated to be 22.4 and 3.3 kcal/mol, which agree well with the experimental values, 24.1 and 3.6 kcal/mol. After the first hydrolysis, the substituted Cl^- is found in the first solvation shell. We also discuss the effect of Cl^- on the second hydrolysis.

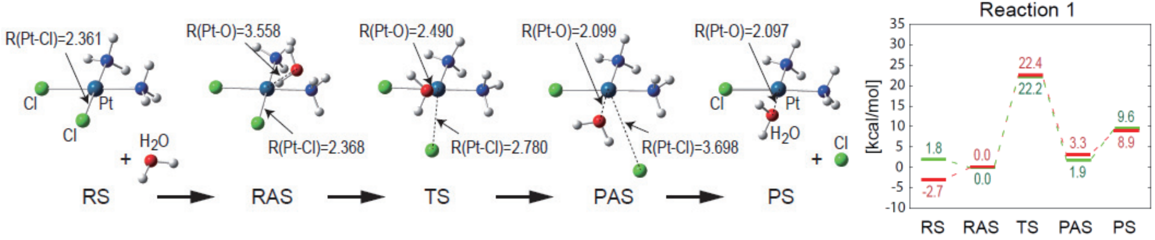


Fig.1 : Geometry and free energy change in the first hydrolysis of cis-platin

Red and green lines are calculated with and without thermo-dynamical correction, respectively.

[1] Mammen, M.; Shakhnovich, E. I.; Deutch, J. M. and Whitesides, G. M., J. Org. Chem. **1998**, 63, 3821

4PP-43

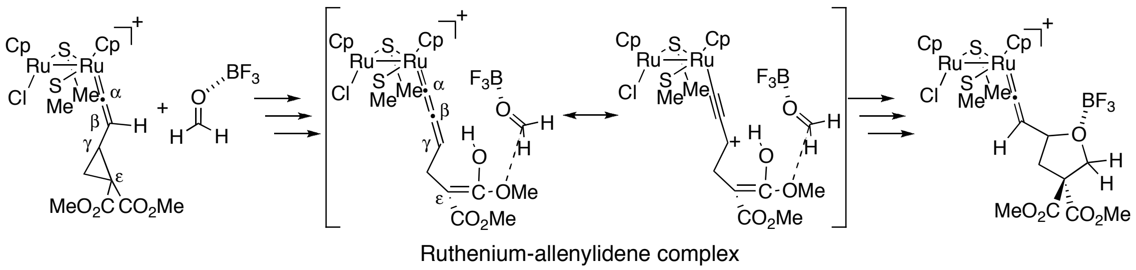
Ruthenium-catalyzed [3+2] cycloaddition via ruthenium-allenylidene intermediate: A DFT study

Ken Sakata,[1] Yoshihiro Miyake,[2] Yoshiaki Nishibayashi[2]
[1]*Faculty of Pharmaceutical Sciences, Hoshi University, Japan*
[2]*Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Japan*

I. Introduction

We have recently found that the ruthenium-catalyzed [3+2] cycloaddition of ethynylcyclopropanes with aldehydes and aldimines gives the corresponding 2-ethynyltetrahydrofuranes or pyrrolidines in high to excellent yields with a high to excellent diastereoselectivity [1]. Experimental results have indicated that the formation of ruthenium–allenylidene complexes via carbon-carbon bond cleavage is one of the most important steps for the catalytic cycloaddition. Thus, we carried out the DFT calculations using B3LYP hybrid functional for the model reaction system (Scheme 1).

Scheme 1.



II. Results and Discussion

The [3+2] cycloaddition has been clarified to proceed smoothly via the ruthenium–allenylidene complex. In the pathway, the transfer of the hydrogen atom at the β-carbon to the oxygen atom in the ester group and the bond cleavage between the γ-carbon and the ε-carbon give the ruthenium–allenylidene complex. Then, the nucleophilic attack of the ε-carbon to the carbonyl carbon atom of formaldehyde occurs with low activation energy. The following some elementary processes give the product complex. The reaction pathway via the ruthenium–allenylidene complex is preferred to the concerted pathway in which the BF_3-coordinated formaldehyde directly attacks the cyclopropane ring in the reactive vinylidene complex. We also discuss the difference between the reaction pathway examined in the present study and the pathway which have been reported for the Lewis acid catalyzed cycloaddition of aldehydes with the donor-acceptor cyclopropanes [2].

[1] Miyake, Y.; Endo, S.; Moriyama, T.; Sakata, K.; Nishibayashi, Y. *submitted.*

[2] Pohlhaus, P. D.; Sanders, S. D.; Parsons, A. T.; Li, W.; Johnson, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 8642.

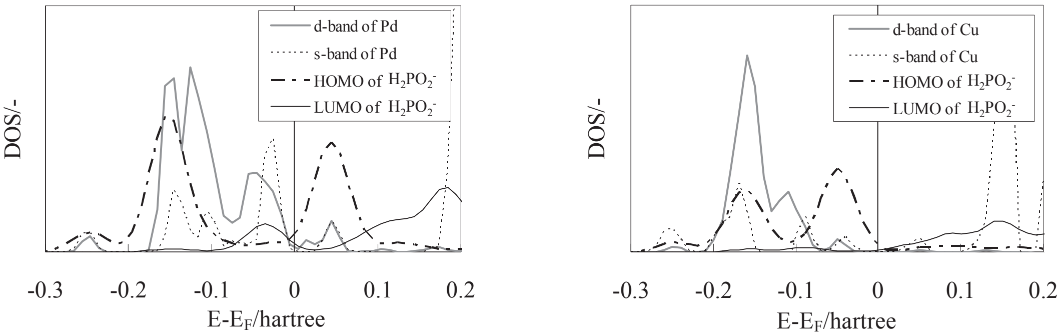
4PP-44

Theoretical Study on Catalytic Activity of Metal Surfaces on P-H Bond Cleavage of Hypophosphite Ion

Masahiro Kunimoto,[1] Hiromi Nakai,[2] Takayuki Homma[1]
[1]Department of Applied Chemistry, [2]Department of Chemistry and Biochemistry,
Waseda University, Japan

Electroless deposition process is technique to form metal thin films using reducing agents as electron supply sources. We have analyzed reaction mechanism of the process theoretically to achieve further precise control[1]. We particularly focus on catalytic activity of metal surfaces on reducing agent reaction, which is one of the most important aspects to control the overall reaction process. It is well known that Pd and Cu each show totally different behaviors in the catalytic activity. In order to elucidate the different behavior, this paper reports interaction structure between metal surfaces, Pd and Cu, and a widely used reducing agent, hypophosphite ion, $H_2PO_2^-$.

It was found that a P-H elongating $H_2PO_2^-$, which is called as “activated $H_2PO_2^-$”, showed characteristic interaction with each metal surface. On Pd, both HOMO and LUMO of activated $H_2PO_2^-$ interact with d-band of Pd to form bonding interactions (Fig.1(a)). On the other hand on Cu, neither HOMO nor LUMO form bonding interaction with orbitals of Cu (Fig.1(b)). HOMO interacts with d-band to form anti-bonding orbital. LUMO interacts with no orbitals of Cu surface. These results indicate that Pd surface activates P-H dissociation of $H_2PO_2^-$, whereas Cu surface does not. The difference is expected to be one of the most important factors to explain the catalytic activity difference between Pd and Cu.



(a) (b)

Fig. 1. Density of states of each molecular orbital (E_F = fermi level) (a) activated $H_2PO_2^-$ and Pd surface, (b) activated $H_2PO_2^-$ and Cu surface

[1] M. Kunimoto, T. Shimada, S. Odagiri, H. Nakai, T. Homma, *J. Electrochem. Soc.*, *in press*

Acknowledgements: This work was performed at the Global Center of Excellence (G-COE) program “Practical Chemical Wisdom” from The Ministry of Education, Culture, Sports, Science and Technology, Japan and was financially supported in part by the Grant-in-Aid for Scientific Research(B).

4PP-45

Towards the development of the TD effective nuclear potential for Time-Dependent Multicomponent Density Functional Theory

Yasumitsu Suzuki,[1] Koichi Yamashita,[1]
Ali Abedi,[2] E. K. U. Gross[2]
[1]*School of Engineering, The University of Tokyo, Japan*
[2]*Max-Planck Institut für Mikrostrukturphysik, Germany*

It is incontestable that developing the efficient computational tractable theory which can treat the nonadiabatic processes is extremely important. To understand the microscopic mechanism of the reactions which evolves on multiple electronic states, such as surface reactions and reactions in intense laser fields, it is extremely important to develop the theory which can treat electron-nuclear correlation properly. Such theory must go beyond the conventional mixed classical-quantum mechanical methods because it is frequent that the quantum nature of nuclei is crucial in these reactions. Furthermore, the conventional nuclear wavepacket propagation method is not sufficient because it needs very heavy computational costs and can only be applied to the system which evolves on few BO potential energy surfaces.

As an appealing new theory to deal with above problems, the extension of Time-Dependent Density Functional Theory (TDDFT) to the multicomponent systems is quite promising. This manifests that one-to-one correspondence between the time-dependent potentials and densities can be established for multicomponent systems. Thus the time-dependent densities of nuclear and electron can be obtained from the time-dependent multicomponent Kohn-Sham equations.

To develop the time-dependent nuclear-electron interaction functional, which is the key factor of this theory, we firstly investigate the time-dependent effective nuclear potential from various theories and analyze what is important to reproduce the exact one.

4PP-46

Molecular dynamics study of the photodesorption process of the CO molecule from the surface of interstellar ice

Marc C. van Hemert,[1] Junko Takahashi,[2] Ewine F. van Dishoeck[3]
[1]*Institute of Chemistry, University of Leiden, The Netherlands*
[2]*Meiji Gakuin University, Japan*
[3]*Leiden Observatory, University of Leiden, The Netherlands*

I. Introduction

At the densities and temperatures in star-forming regions, all molecules other than H_2 should be kept frozen on dust grains within the timescales shorter than the interstellar cloud lifetimes. But, gaseous CO is detected there. Thermal desorption is negligible and thus photodesorption has been suggested as a possible mechanism. In the laboratory, this process has been simulated by depositing CO on a 10 K surface and following CO desorption upon irradiation of a D_2 discharge lamp [1]. In order to study this process theoretically, we performed classical molecular dynamics simulations of the CO molecule excited with a photon on the surface of amorphous CO crystals.

II. Method

For the ground state interaction potential of the CO-CO dimer, we performed ab initio CCSD calculations on a large grid of orientations and inter- and intra- molecular distances. We fit about 15000 data points to the interaction energy formula including the repulsive potential with the nonlinear alpha parameters, the dispersion potential, and the electrostatic potential. For the excited state, we used the contracted CI method where the two CO molecules lie in the same plane, the first CO has the ground state equilibrium bond length, and the second CO has a bond length close to the $A^1\Pi$ excited state one. We fit these data to the formula similar to the one used for the ground state, although we excluded all OCCO geometries.

We created amorphous CO crystals consisting of 200-1200 CO molecules. The initial geometries were determined by adding CO molecules one by one to the energetically most favored positions with a simplex method. These crystals were modified by the molecular dynamics procedure of temperature cycling with the steps from 0 to 50 K and back to 10 K for 10000 cycles with 20 au (~0.5 fs) time step. Then, we brought a selected flake of the CO crystal into the excited state adiabatically with a photon of 9.1-9.9 eV. After the dynamics for 5000-10000 cycles with 4 au (~0.1 fs) time step, we brought back the flake into the ground state adiabatically and monitored the positions of CO molecules for another 50000 au.

III. Results and discussion

We found that only 5-10% of the excited CO molecules were photodesorbed from the CO crystal. Of the total number of desorbed molecules, 20-25% were neighboring molecules (3.5-4.0 Bohr), and a few percent next-neighboring ones (6.5-7.0 Bohr). There was little effect of photon energy. The effect of the flake size was that the larger the flake, the stronger molecules were bound in the surface layer of the CO crystal. We found that almost all of the molecules directly desorbed came from the surface layer, and that the surface layer molecules were also kicked out by the excited neighboring molecules in the subsurface layer.

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4PP-47

Theoretical study of bifurcating reactions accompanying the totally-symmetric valley-ridge inflection point

Yu Harabuchi[1] and Tetsuya Taketsugu[2]
[1] *Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan*
[2] *Graduate School of Science, Hokkaido University, Japan*

Introduction

In theoretical study of chemical reactions, an intrinsic reaction coordinate (IRC) has played a significant role for understanding the reaction mechanism. Since the IRC belongs to the totally-symmetric irreducible representation of the molecular point group, the reaction coordinate has no curvature coupling with the transverse normal coordinates of non-total-symmetry, and thus the intrinsic reaction path (IRP) starting from TS sometimes reaches the second TS through the non-totally-symmetric VRI point. If a non-totally-symmetric VRI appears on the IRP and the second TS is detected at the terminal, this TS connects two symmetrically equivalent product minima with the lower symmetry. As to non-totally-symmetric VRI, there have been a lot of theoretical studies.

On the other hand, when there appears the totally-symmetric VRI point, the reaction pathway can bifurcate, leading to two completely different product minima. In the target reaction (Fig.1), it was shown that IRC calculations from the transition state (ET-TS) lead to different product minima, SUB(C) and (C_{ET}) [1], by using non-mass-weighted internal coordinates and mass-weighted Cartesian coordinates, respectively. *Ab initio* molecular dynamics simulations were also performed to discuss the branching ratio of the products [2]. From the viewpoint of bifurcating reactions, it is very interesting that two different sets of products could be generated.

To clarify the mechanism of bifurcation, we performed geometry optimizations of stationary points and IRC calculations for the reactions $XCHO^-$ + CH_3Cl (X = H, CH_3) at the MP2/6-31+G(d) level. We also applied a projection technique to obtain vibrational frequencies, the Mulliken net charge and spin population of each atom, as well as the energy of the first-excited state, along the IRP. All calculations were performed using the GAMESS program package.

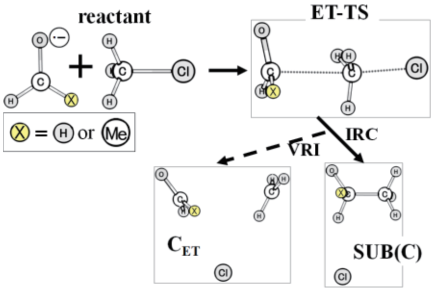

Figure 1. The reaction scheme of $H(X)CO^-$ + CH_3Cl (X = H, Me)

Results and Discussion

The IRC calculation from ET-TS leads to SUB(C) at the MP2/6-31+G(d) level. It is shown that the VRI point at the HF level [1] disappear in a system of X = H at the MP2 level. On the other hand, in the second reaction (X = CH_3), it is verified that the IRP has the totally-symmetric VRI point leading to two different product minima on the PES. In the same region of the totally-symmetric VRI point, the reaction-path tangent vector changes its direction drastically in a local region. We concluded that the change of the IRP curvature is strongly related to the bifurcation [3].

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[3] Y. Harabuchi and T. Taketsugu, *Theo. Chem. Acc.*, in press (2011).

4PP-48

Photodissociation, geminate recombination, and vibrational relaxation of iodine in carbon tetrachloride: A molecular dynamics simulation

Jakob Petersen, Niels E. Henriksen, Klaus B. Møller
CMM – Centre for Molecular Movies, Department of Chemistry,
Technical University of Denmark

The photodissociation, subsequent geminate recombination, and vibrational relaxation of iodine in carbon tetrachloride are studied using classical nonequilibrium molecular dynamics simulations. The time-dependence of the vibrational relaxation associated with the cooling of iodine in the electronic ground state is found to be in good agreement with previous experimental results. We show that the relaxation exhibits some degree of coherence even at 10 ps after laser excitation, and that a good approximation to the time-dependent I-I distribution function can be extracted from the time-dependent vibration energy distribution. Hence, experimental results from time-resolved x-ray diffraction and optical spectroscopy studies can be compared.

4PP-49

Theoretical study on dehydrogenation reaction of methanol on anionic Au cluster

Karan Bobuatong,[1] Sangita Karanjit,[2] Masahiro Ehara[1], Hidehiro Sakurai[2]
[1]Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan
[2]Institute for Molecular Science 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Japan

The aerobic oxidation of methanol to formic acid catalyzed by Au_{20}^- has been systematically investigated quantum chemically using the M06 density functional. The proposed reaction mechanism consists of three elementary steps: (1) formation of formaldehyde from methoxy species activated by superoxo-like anion on gold cluster; (2) nucleophilic addition by hydroxyl group of hydroperoxyl-like complex to formaldehyde leading to a hemiacetal intermediate and (3) formation of formic acid by hydrogen transfer from hemiacetal intermediate to atomic oxygen attached to gold cluster. A comparison of the computed energetics of various elementary steps indicates that the C-H bond dissociation of methoxy species leading to formation of formaldehyde is the rate-determining step. A possible reaction pathway involving single-step hydrogen abstraction, concerted mechanism, is also discussed. The stability of reactants, intermediates and transition structures are governed by coordination number of gold atoms, charge distribution, cooperative effect and structural distortion which are the key parameters for understanding the relationship between structure of gold cluster and catalytic activity of the aerobic oxidation of alcohol.

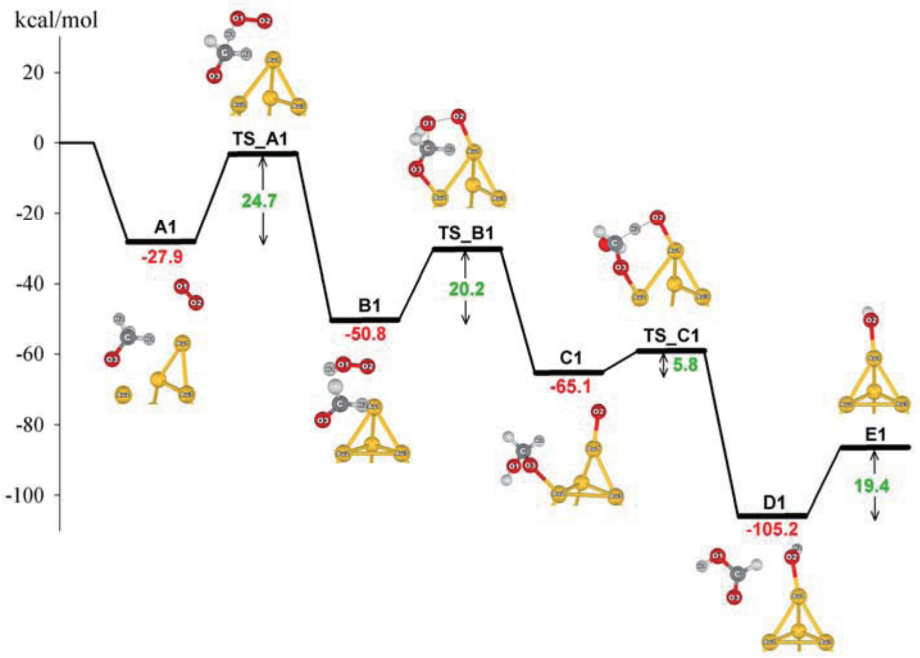


Figure 1. Reaction pathways of the aerobic oxidation of methanol to formaldehyde on Au_{20}^-.

4PP-50

Molecular dynamics simulations of azanaphthoquinone annelated pyrrole derivatives as anti-cancer agent in DNA duplex

Pornpan Pungpo[1], Auradee Punkvang[1], Amonrat Kumkong[1], Parit Khamsri[1],
Patchreenart Saparpakorn[2], Nipawan Pongprom[1],
Peter Wolschann[3] and Supa Hannongbua[2]
[1]*Department of Chemistry, Faculty of Science, Ubonratchathani University, Ubonratchathani, Thailand*
[2]*Department of Chemistry, Faculty of Science, Kasetsart University, Chatuchak, Bangkok, Thailand*
[3]*Institute for Theoretical Chemistry, University of Vienna, A-1090 Vienna, Austria*

Abstract

To discover the new anti-cancer agent with high activity and low side effect, azanaphthoquinone annelated pyrrole derivatives, a class of the synthetic DNA intercalating agent have been synthesized. These compounds exhibit high cytotoxic activity against tumor cell lines. However, the binding modes of these anti-cancer agents have not been investigated. In order to predict the potential binding modes of these compounds in DNA duplex, molecular dynamics (MD) simulations with AMBER program were performed. Moreover, to calculate the binding free energy of azanaphthoquinone annelated pyrrole derivatives in DNA binding site MM-PBSA method was employed. Based on MD simulations, azanaphthoquinone annelated pyrrole scaffolds of azanaphthoquinone annelated pyrrole derivatives are inserted into two base pair steps of cytosine (C) and guanine (G). The π-π interaction azanaphthoquinone annelated pyrrole scaffold with base pairs of C and G is the crucial interaction for binding of these anti-cancer agents. Moreover, the hydrogen bond interaction of R substituents reinforces the binding of these compounds. Based on the calculated binding free energy, the hydrogen bond interaction of R substituent could enhance the binding affinity of azanaphthoquinone annelated pyrrole derivatives in DNA duplex. Therefore, the obtained results should be helpful for understanding the binding modes and the crucial interactions of azanaphthoquinone annelated pyrrole derivatives in DNA binding site. This information benefits for designing the novel anti-cancer agent with high activity and low side effect.

Molecular modeling on anti-tuberculosis agent to investigate the structural basis for improving potency against *M. tuberculosis* strain

Auradee Punkvang[1], Patchareenart Saparpakorn[2], Peter Wolschann[3],
Supa Hannongbua[2] and Pornpan Pungpo[1]
[1] *Department of Chemistry, Faculty of Science, Ubonratchathani University, Ubonratchathani, Thailand*
[2]*Department of Chemistry, Faculty of Science, Kasetsart University, Chatuchak, Bangkok, Thailand*
[3]*Institute for Theoretical Chemistry, University of Vienna, A-1090 Vienna, Austria*

Abstract

The tuberculosis treatment still remains the worldwide medical problem because of the drug resistance. The enoyl-ACP reductase (InhA) from *M. tuberculosis* is an attractive target for developing new antibiotic agents and has been identified as the target of isoniazid (INH), a first-line antibiotic for tuberculosis treatment. The high potency of INH is diminished by the drug-resistance. To overcome the drug-resistant problem of INH, arylamides as the direct InhA inhibitor have been identified. In this study, molecular modeling approaches were employed to elucidate inhibitor-enzyme interactions and structural basis for improving the affinity and potency of anti-tuberculosis agents in class of isoniazid derivatives and arylamide derivatives. Molecular docking calculations and QSAR methods were applied on series of isoniazid and arylamide derivatives to gain an insight into the structural basis for improving anti-tuberculosis activity. Moreover, to investigate the dynamics behaviors in the term of flexibility, structural features and ligand-enzyme interactions of anti-tuberculosis agent in InhA binding site, molecular dynamics (MD) simulations were employed. The integrated results from this study provide coincident information about the inhibitor-enzyme interaction and structural requirement thus offering guidelines for the synthesis of novel anti-tuberculosis agent with highly antibiotic activity.

4PP-52

STUDY ON THE MECHANISM FOR THE REACTION OF PBP2a WITH BETA-TACLAM INHIBITORS BY ONIOM METHOD

Nguyen Hoa My(1), Hirao Hajime(2), Dang Ung Van(1), Keiji Morokuma(2)
(1)Center for Computational Chemistry, Faculty of Chemistry, Ha Noi University of Science, Vietnam
(2)Fuikui Intitute of Fudamental Chemistry, Kyoto University, Japan

Abstract

Mechanisms of drug resistance constitute a very complicated research subject attracting scientists in Vietnam and many other countries all around the world. We have calculated the mechanism of the Michaelis complex formation reactions between small β-lactam molecules (i.e. Methicilin and Nitrocefin) and PBP2a using the ONIOM(B3LYP/6-31G*:AMBER) hybrid quantum mechanical/molecular mechanical (QM/MM) method. Active-site model calculations at the B3LYP/6-31G* level have also been performed. All calculations have been performed on High Performance Computation System. This is the first time the ONIOM was applied to the reaction of PBP2a with β-lactam inhibitors. In the ONIOM models, two systems (or layers) were defined for the entire system: the model system (the first layer) which was calculated by the B3LYP method with the 6-31G* basis set and the real system was calculated with the AMBER force field. The calculations ~~shows~~ that the reaction mechanism involves at least two transition states One of them is associated with C-O bond formation. The protein environment significantly increased the activation energy of the acylation reaction. The details are discussed in the presentation.

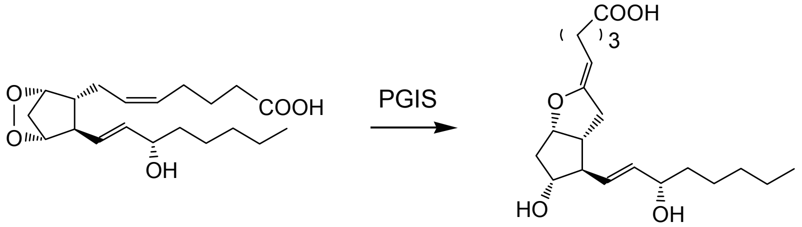
4PP-53

Molecular Dynamics Study on Complex between Prostacyclin Synthetase and Prostaglandin H_2

Ryo Watanabe, Yoshimura Takayoshi, Seiji Mori
Faculty of Science and Engineering, Ibaraki University, Japan

I. Introduction

Cytochrome P450 is a group of heme proteins widely distributed from microorganism to plants and animals in the living world and is one of the important group of enzymes involved in drug metabolisms and syntheses of steroids in vivo. Typical reactions catalyzed by P450 are monooxygenation reactions. One is prostacyclin synthase (PGIS), which catalyzes an isomerization reaction from prostaglandin H_2 (PGH_2) to prostacyclin (PGI_2). PGIS doesn't need any O_2 nor NAD(P)H.

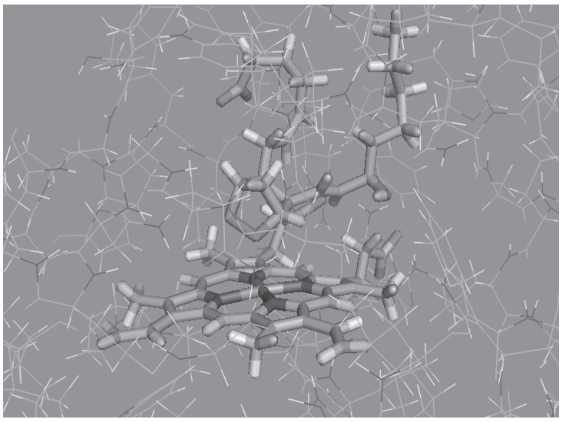


Prostaglandin H_2 (PGH_2) Prostacyclin (PGI_2)

The isomerization reaction mechanism was proposed based on density functional studies by our group. 1) However, these studies haven't considered the effect of protein and solvent.

II. Method and Result

The crystal structure of human Prostacyclin Synthase (PGIS) binding an inhibitor minoxidil (PDB:3B6H （Resolution: 1.62 Å)） is used. After we have deleted a minoxidil from PGIS, We manually placed PGH_2. This initial conformation of the PGH_2 structure was taken from a liternature based on NMR structural analyse.2) After we performed molecular dynamics simulation method (Program: Amber ver.10, ff03 force field, NPT ensemble, 300K). Results were obtained with the substrate-heme coordination structure. Around the catalytic pocket we found only a number of water molecules.



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1) Yanai, T. K.; Mori, S; *Chem. Eur. J.* **2009**, *15*, 4464-4473.
2) Ruan, K.H.; Wu, J; Cervantes, V. *Biochemistry* **2008,** *47,* 680-688.

4PP-54

Computational analysis for DNA religating reaction by E.coli topoisomerase IA

Kyohei Hanaoka,[1] Daiki Kondo,[1] Moonyoung Yang, [1] Katsumasa Kamiya, [1]
Mitsuo Shoji[2], Kenji Shiraishi[1]
[1]*Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan*
[2]*Center for Computational Science, University of Tsukuba, Japan*

I. Introduction

DNA topoisomerase IA cleavages and religates a single strand DNA to relax the DNA super coil and promotes DNA metabolism. Inhibition of this function is known to lead to bacterial cell death. Thus, this enzyme is expected as a potent antibiotic target. This enzyme forms a covalent intermediate in which catalytic tyrosine residue is covalently bonded to the DNA backbone phosphate, after and before cleavage and religation reaction. Thus the covalent intermediate is a key state in the catalytic mechanism of religating for DNA topoisomerase IA. Recently, the crystal structure of the covalent intermediate of E. coli topoisomerase IA in complexed with single strand DNA was solved at 2.3A resolution (Figure.1) [1]. However, this structure does not reveal overall detail of the catalytic site of the religation reaction. This is because, to capture intermediate, Asp111 in the catalytic site was mutated to Asn and divalent magnesium ion, which is needed to the religation reaction, was neutralized by chelator. Therefore, computational approaches are needed to complement the structure around the catalytic site of religation reaction and reveal hydrogen bonding and salt bridge networks which may contribute to the catalysis.

II. Computational study

In this study, we started from the crystal structure of covalent intermediate of DNA topoisomerase IA in complexed with DNA substrate (PDB ID; 3PX7). We first modeled Asp111 which has been mutated to Asn and added divalent magnesium ions to small cavity around its catalytic site. Next we performed molecular dynamics simulation to determine the position of divalent magnesium ions and structure of hydrogen bonding networks around the catalytic site. And then, we performed DFT (density functional theory) calculations to reveal the catalytic mechanism of the religation reaction. In the session, we will discuss about roles of the individual components contained in the catalytic site.

Fig.1 Crystal structure of
the covalent intermediate of
E. coli DNA topoisomerase IA

4PP-55

Density functional study of electronic structures of a characteristic [4Fe-4S] cluster, [$Fe_4S_4(SCH_3)_3(CH_3COO)$], in dark-operative protochlorophyllide oxidoreductase

Yu Takano,[1] Yasushige Yonezawa,[1] Yuichi Fujita,[2] Genji Kurisu,[1] Haruki Nakamura[1]
[1]*Institute for Protein Research, Osaka University, Japan*
[2]*Graduate School of Bioagricultural Sciences, Nagoya University, Japan*

The [4Fe-4S] clusters are ubiquitous in nature and play important roles in electron transfer and catalysis such as in ferredoxins and nitrogenases. Recently, a X-ray structure of the dark-operative protochlorophyllide oxidoreductase (DPOR) has been determined at 2.3 Å resolution [1]. The [4Fe–4S] cluster in DPOR (NB cluster) has such a characteristic structural feature that one of the iron ions is chelated by the carboxylate group of Asp36, unlike conventional [4Fe-4S] clusters coordinated with four Cys residues. To examine the effect of the Asp ligation on the enzymatic activities, three NB-protein mutants, D36C, D36S, and D36A, were prepared. Although the D36C and D36S substitutions almost nullified the activity, the D36A mutant exhibited 13 % of the wild-type level. The crystal structures of the D36C mutant was found to have the conventional [4Fe–4S] cluster coordinated with four Cys residues, while that of the D36A mutant had a [4Fe–4S] cluster chelated by three Cys residues and an unknown fourth non-protein ligand, which was likely to be the hydroxide or chloride ion. These findings indicate that Asp ligation is important for the enzymatic activity.

In this study, we have explored the electronic structure of the NB cluster to elucidate the role of the Asp ligation to the [4Fe–4S] cluster in the catalysis of DPOR using the density functional theory (B3LYP) [2]. The electronic structure of the NB cluster is compared with those of the conventional [4Fe–4S] clusters in the D36C variant and the putative [4Fe–4S] clusters in the D36A mutant. Although the electronic structures are similar to each other, our computation shows that the redox potential of the NB cluster is lower than that of the D36C model in the 2–/3– reduction reaction, in an environment with the dielectric constant higher than 10, showing that the NB cluster can transfer an electron more easily than the conventional [4Fe–4S] cluster. This redox character demonstrates the important role of Asp36 in DPOR. It is also found that the electron-donating character of the [4Fe–4S] clusters in the 2–/3– reduction in an environment with high dielectric constant is in the same order as the experimental enzymatic activities of the wild type DPOR and its mutant, indicating that the fourth ligand of the [4Fe–4S] cluster in the D36A mutant is likely to be a chloride ion.

[1] N. Muraki, J. Nomata, K. Ebata, T. Mizoguchi, T. Shiba, H. Tamiaki, G. Kurisu, Y. Fujita, Nature 465 (2010) 110–114.
[2] Y. Takano, Y. Yonezawa, Y. Fujita, G. Kurisu, H. Nakamura, Chem. Phys. Lett. 503 (2011) 296–300.

Ab inito study on triplet excitation energy transfer in photosynthetic light harvesting complexes

Zhi-Qiang You,[1,2,3] Chao-Ping Hsu,[2]
[1] *Taiwan International Graduate Program and* [2] *Institute of Chemistry, Academia Sinica, 128 Section 2 Academia Road, Nankang, Taipei 11529, Taiwan*
[3] *Department of Chemistry, National Tsing Hua University, 101 Section 2 Kuang-Fu Road, Hsinchu 30031, Taiwan*

We have studied the triplet energy transfer (TET) for photosynthetic light-harvesting complexes, the bacterial light-harvesting complex II (LH2) of *Rhodospirillum molischianum* and *Rhodopseudomonas acidophila*, and the peridinin-chlorophyll *a* protein (PCP) from *Amphidinium carterae.* The electronic coupling factor was calculated with the recently developed fragment spin difference scheme (You and Hsu, *J. Chem. Phys.* **2010**, *133*, 074105), which is a general computational scheme that yields the overall coupling under the Hamiltonian employed. The TET rates were estimated based on the couplings obtained. For all light-harvesting complexes studied, there exist nanosecond triplet energy transfer from the chlorophylls to the carotenoids. This result supports a direct triplet quenching mechanism for the photoprotection function of carotenoids. The TET rates are similar for a broad range of carotenoid triplet state energy, which implies a general and robust TET quenching role for carotenoids in photosynthesis. This result is also consistent with the weak dependence of TET kinetics on the type or the number of π conjugation lengths in the carotenoids and their analogs reported in the literature. We have also explored the possibility of forming triplet excitons in these complexes. In B850 of LH2 or the peridinin cluster in PCP, it is unlikely to have triplet exciton since the energy differences of any two neighboring molecules are likely to be much larger than their TET couplings. Our results provide theoretical limits to the possible photophysics in the light-harvesting complexes. This work has been published in *J. Phys. Chem. A* **2011**, *115*, 4092.

4PP-57

Quantum Chemical Study on Molecular-Level Affinity of DJ-1 Binding Compounds

Yasuhiro Shigemitsu[1]
[1]*Industrial Technology Center of Nagasaki, Japan*

I. Introduction

DJ-1 is a 20-kDa protein comprising 189 amino acid residues ubiquitously expressed in various human tissues. The multifunctional protein plays essential roles in tissues with higher order biological functions. Of the versatile functions, a mutation of DJ-1 was found to be responsible for familial Parkinson's Disease (PD). Superfluous oxidation of cysteine at amino acid 106 (Cys106) renders DJ-1 inactive, and such oxidized DJ-1 has been observed in patients with the sporadic form of PD [1]. This presentation aims to elucidate the structure-function relationship of DJ-1 through a series of computational chemistry analysis.

II. Results and Discussion

The active (reduced) and inactive (oxidized) PDB structures were extracted from 1UCF and 1SOA, respectively. The starting structures were adequately modified and further refined through energy minimization and equilibrium steps by means of AMBER molecular dynamics program. The obtained structures were analyzed for the active site around Cys106 in HF-FMO/6-31G(d) level of theory by using Fragment Molecular Orbital method implemented in GAMESS-US software.

The FMO analysis indicates the subtle change of the active site's environment. The closely contacted residues (Arg156,Glu18,Gly75,His126) alter its relative positions in response to the oxidation to Cys106. The interaction mechanism between DJ-1 and binding compounds is discussed based on FMO and MM-PBSA analysis.

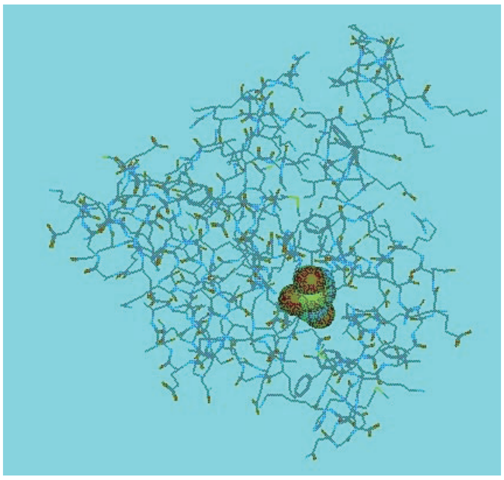

Figure 1. 1SOA structure (CPK-highlighted)

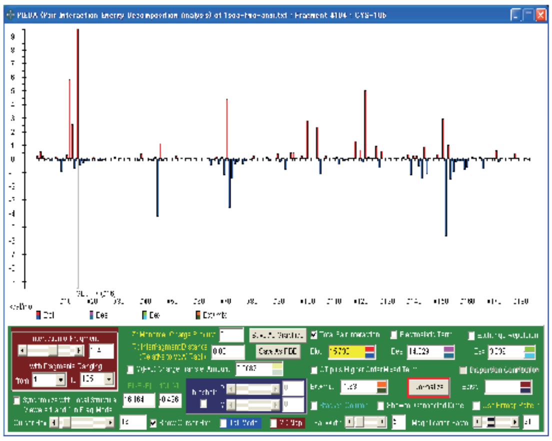

Figure 2. PIEDA for 1SOA

[1] S.Miyazaki, H.Ariga et al, J.Nurochemistry, Vol.105, pp.2418-2435 (2008)

4PP-58

Theoretical study on hydrated DNA systems by linear-scaling DFT code CONQUEST

Takao Otsuka,[1] Tsuyoshi Miyazaki,[2] David R. Bowler,[3] Michael J. Gillan,[3]
[1]*Quantitative Biology Center(QBiC), RIKEN, Japan*
[2]*National Institute for Materials Science, Japan*
[3]*University College London, London, United Kingdom*

We present our theoretical study on hydrated DNA system by using the linear scaling (or order-N (O(N)) density functional theory (DFT) code CONQUEST. The system we calculated consists of 3439 atoms (634 atoms for a DNA of d(CCATTAATGG)$_2$ (PDB code 1WQZ), 9 Mg counter ions and 932 water molecules).

We have found that our O(N) DFT methodology is robust and accurate. The dependence of the total energy on the cutoff radius of the (auxiliary) density matrix is shown in figure 1 and we can see that the energy converges very rapidly. We have also compared the atomic forces and the total energies calculated by CONQUEST with those by AMBER. Figure 2 shows the force components for the atoms of Ade3 part, which includes the atom having the largest force components. We find that these two methods show semi quantitative agreements for these atoms. Figure 3 shows the comparison of the total energy differences between CONQUEST and AMMBER. The van der Waals interaction seems to improve the total energy differences. The results on another DNA system will be also reported.

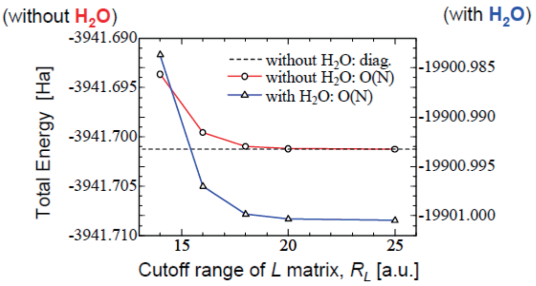

Figure 1. Dependence of total energy on cutoff length R_L of the auxiliary density matrix in O(N)

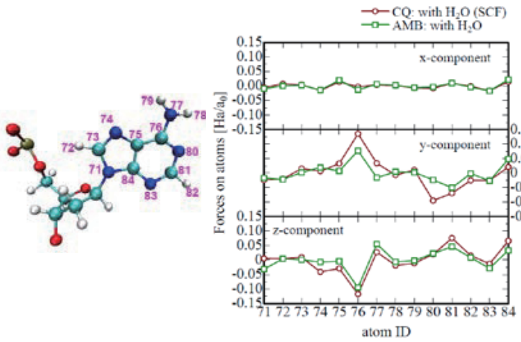

Figure 2. Atomic force components calculated by CONQUEST and AMBER for the atoms of Ade3 part.

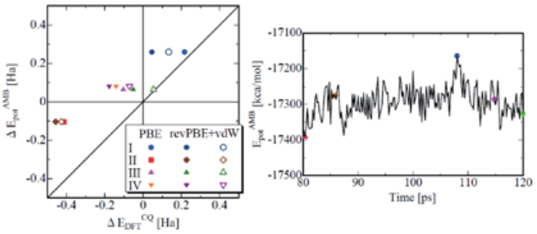

Figure 3. Comparison of total energy differences between CONQUEST and AMBER

[1] T. Otsuka, T. Miyazaki, T. Ohno, D. R. Bowler, M. J. Gillan, J. Phys. Condens. Matter **20**, 29401 (2008).

[2] T. Otsuka, T. Miyazaki, D. R. Bowler, M. J. Gillan, to be appeared.

4PP-59

Electronic excited state of a series of porphyrin molecules; Development of an effective renormalization scheme

Masaaki Saitow, Yuji Mochizuki
Department of Chemistry and Research Center for Smart Molecules, Rikkyo University, 3-34-1 Nishi-ikebukuro, Toshima-ku, Tokyo 171-8501, Japan

I. Introduction

The porphyrin derivatives including chlorophyll and bacteriochlorophyll play the central role on the light reaction in the photosynthesis, by catching the energy of photon. Such the molecules possess the highly conjugated MOs, and vary its spectral behavior depending on the substituent groups, structures and the environmental effects by the surrounding residues. By favor of this property, this kinds of molecules are able to absorb almost whole range of a solar radiation. Moreover, it is pronounced these species show sharp peak at about 3 eV, known as B- or Soret-band and the corresponding quantum yield reaches ∼100%. The other characteristic peak is located at nearly 2 eV, on the other hand, which is termed as Q-band with the far smaller oscillator strength. From such attractive bio-chemical and -physical aspects, there have been countless theoretical efforts for the accurate description of porphyrin derivatives such based on as DFT/MRCI[1], SAC-CI[2], and EOM-CCSD[3]. These methodologies have been considered more preferable to the lower order variants like CIS(D) because of the closely degenerated character, doubly- and triply-excited configurations predominantly account for up to ∼30%.

Then, our objective is to accomplish a theoretical approach that can be applicable for even such the species, by utilizing effective renormalization techniques composed of a so-called partial-renormalization[4] for the differential correlation term, and a self-energy shifting for the orbital relaxation term. The order of the formulas is seized at merely the second order.

II. Brief explanation of the results

The excitation energies for zinc-porphyrin (ZnP) are showed in the table below, where CIS, CIS(D) and ADC(2) values were obtained with 6-31G*[6d/10f] basis set using our local version of PSI3 quantum chemistry program suite. It is readily recognizable the single reference values were affected by the multireference character of ZnP, which resulted in insufficient agreement with the observed values.

The excitation energies, and corresponding oscillator strengths shown in parentheses for ZnP calculated by various methodologies and the observed values.

	CIS	CIS(D)	ADC(2)^a	DFT/MRCI*	SAC-CI**	Obs.
1^1E_u	2.54(0.0442)	2.79	2.53(0.0000391)	2.21(0.0050)	1.84(0.0129)	2.28*
2^1E_u	4.75(2.61)	3.47	3.59 (2.47)	3.28(1.27)	3.50(3.38)	3.04, 3.22, 3.05*

*, ** These are from Ref.[1] and [2], respectively, and references therein.

^{a} Oscillator strengths were calculated using ordinary dipole integral, instead of the generalized matrix element.

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[4] C. E. Dykstra, and E. R. Davidson, Int. J. Quantum Chem. **78**, 226 (2000).

4PP-60

Interaction analysis of HIV-1 antibody 2G12 and glycans using FMO calculations

Yuka Koyama[1], Kaori Ueno-Noto[2] and Keiko Takano[1]
[1]*Graduate School of Humanities and Sciences, Ochanomizu University, Japan*
[2]*College of Liberal Arts and Sciences, Kitasato University, Japan*

Ⅰ. Introduction

Human antibody 2G12 is capable of recognizing the high-mannose glycans on the HIV-1 surface glycoprotein, gp120 [1]. Doores *et al.* found that Fab-2G12 bound D-fructose and C-6 methyl mannose stronger than D-mannose [2]. Details of the antibody-neutral carbohydrate ligand interaction are still unclear. To investigate the affinity of Fab 2G12 for glycans, we carried out the interaction energy analysis by ab initio fragment molecular orbital (FMO) calculations [3].

Ⅱ. Method

The FMO calculations at the MP2/6-31G(d) level were performed for various glycan-Fab 2G12 complexes to analyze the difference in binding energy due to the glycan structures, D-mannose, D-fructose, C-5 or C-6 alkyl-substituted mannose, and C-6 methyl tetra mannose. The crystal structures of 2G12 and those glycan ligands were utilized as calculation models (PDB ID: 1OP5, 1OP3, 3OAY, 3OAZ, 3OB0). To evaluate the nature of the interaction energy, pair interaction energy decomposition analysis (PIEDA) was applied, results of which were compared with experimental results [2].

Ⅲ. Results and discussion

Pair interaction energies are shown in Figure 1. Results of glycan **c**, **d** and **e** accord with the experimental data [2]. It was found that electrostatic interaction plays a dominant role in stability and exchange interaction is a major destabilization factor. In contrast, glycan **a** and **b** underestimated the affinity compared with the experimental results, which suggests the significance of water molecules which exist at the binding site in the crystal structures. We further investigated how the water molecules affect the antibody-glycan interaction by analyzing the models containing water molecules.

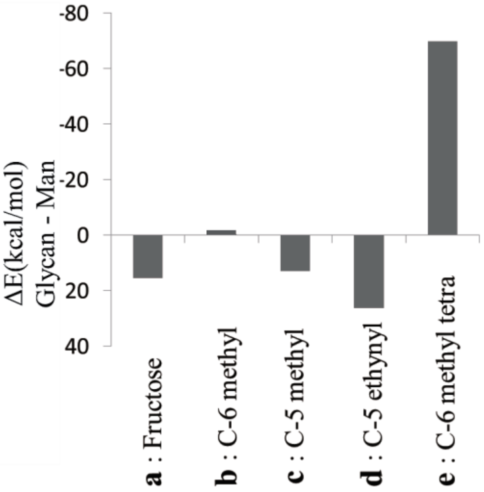


Figure 1. Total pair interaction energy between Fab 2G12 and glycans relative to mannose (kcal/mol)

[1] D. A. Calarese *et al*. *Science* 2003 **300**, 2065. [2] K. J. Doores *et al*. *PNAS* 2010, **107**, 17107. [3] D. G. Fedorov, K. Kitaura, *J. Phys. Chem. A*, 2007, **111**, 6904.

4PP-61

Fragment-DFT calculation on the interaction energy between HIV-1 protease and its inhibitor

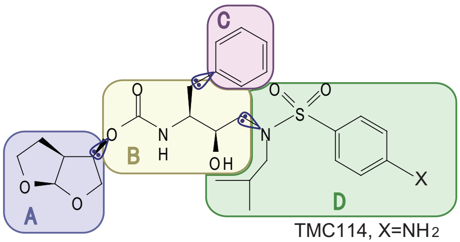
Tomoyuki Iwase, Kenji Morihashi
Department of Chemistry, Graduate School of Pure and Applied Sciences,
University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

I. Introduction

The human immunodeficiency virus type 1 protease (HIV-1 PR) is a main target to develop the anti-AIDS drugs. The main action of HIV-1 PR is to divide a large protein which is the precursor of HIV. Two residues, Asp25 and Asp125, are known for the active site of this action[1]. In this paper, the interaction energy between HIV-1 protease and its inhibitor was calculated by fragment density functional theory (F-DFT)[2], where five inhibitors, TMC114, TMC126, DMP323, indinavir, and lopinavir, were investigated, and were divided into several fragments as fig. 1. Thus, we could estimate the interaction energy on each part of inhibitors. Especially, TMC126 highly resembles TMC114, but has the greater inhibitive capacity than TMC114. Using these methods, we aim to reveal which substituent of HIV-1 protease inhibitor is important to obstruct the HIV-1 protease.

II. Results

The inhibitor-protease binding energies were predicted at the B3LYP level of theory with the 6-31G basis set. The interaction energy calculation shows that the end part of inhibitor generally attracts the P2 binding pocket[3] (Asp28, Asp29, Asp30, Ile50 and corresponding B chain residues), and the hydroxyl group placed on center of inhibitor is attractive with active site Asp25 of HIV-1 protease. TMC126 is more attractive with ASP130 than TMC114 at the fragment D, as shown in fig.2. This is due to the difference of a substituent, which could cause the good inhibitive capacity of TMC 126.



TMC114, X=NH_2
TMC126, X=OMe

fig.1 Fragmentation of TMC114 and TMC126

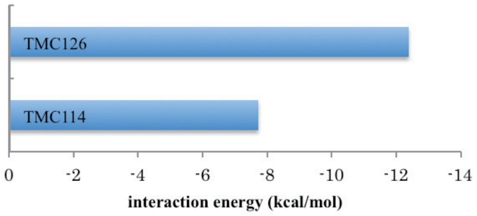


fig.2 Interaction energy between fragment D and ASP130

[1] J. Trylska et al., *Protein Sci.*, **13**, 513(2004) .
[2] Y. Shimodo et al., *J. Mol. Struct.(Theochem)*, **770**, 163(2006).
[3] K. Nivesanond et al., *Int. J. Quantum Chem.*, **105**, 292(2005) .

4PP-62

Theoretical study on the Photo-decarboxylation mechanism of Green Fluorescent Protein

Lina Ding, Lung Wa Chung, Keiji Morokuma*

Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto Japan

Wild-type green fluorescent protein (GFP), discovered from *Aequorea victoria* jellyfish, and its variants have revolutionized GFP technology to visualize molecular events that occur within living cells.[1-3] The absorption spectrum of WT-GFP at pH 8.0 shows two major peaks at 397 nm (A band) and 475 nm (B band) corresponding to neutral and anion forms of the chromophore, respectively. After durative UV/Visible light, photocoversion can occur which was discovered shortly after the cloning of the *gfp* gene. [4, 5] Mechanistic study on this photoconversion based on different techniques separately supported that reversible and irreversible changes can take place, presumably occurring together but expected to have different kinetics and quantum yields. [6]

In this work, systematic high-level ab initio QM and ONIOM (QM:MM) calculations were performed to delineate the possible decarboxylation mechanism involving intra- and inter-molecular charge-transfer(CT) excited states. The calculations support that the decarboxylation process is initiated with the intramolecular CT excited state within the GFP chromophore and then accesses to a conical intersection (CI) channeling to the inter-molecular CT excited state. The intermolecular CT excited state plays a key important role in the photo-induced irreversible process, and finally decays to the ground state via the second CI.

Refs:

1. Tsien, R.Y., *Ann. Rev. Biochem*, **1998**, 67, 509.
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5. Cubitt, A.B., et al., *Trends. Biochem. sci*, **1995**, 20, 448.
6. van Thor, J.J., et al., *J. Bio. Chem* **2005**, 280, 33652.

4PP-63

Effects of phospholipid bilayers on the hydrated excess proton behavior: A computational study

Takefumi Yamashita[1] and Gregory A. Voth[2]

[1]*Laboratory for Systems Biology and Medicine, Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1, Komaba, Meguro, Tokyo 153-8904, Japan*
[2]*Department of Chemistry, James Franck Institute, Institute for Biophysical Dynamics and Computational Institute, University of Chicago, 5735 S Ellis Ave., Chicago, Illinois 60637, United States*

I. Introduction

Proton transport near the phospholipid bilayers is an important and challenging issue in both biophysics and physical chemistry. In this work, we performed atomistic molecular dynamics (MD) simulations in order to study the effects of lipid bilayers on the hydrated excess proton behavior.

II. Methods

In order to describe the proton behavior realistically, the third generation of the multistate empirical valence bond (MS-EVB3) model [1] was adopted. Thus, the characteristic Grotthuss shuttling of the hydrated excess proton is reasonably reproduced in the MD simulations. We studied not only the DOPC bilayer but also the DOPE bilayer and DOPG bilayer in order to investigate the effects of the head group species.

III. Results

Whereas the excess proton forms a hydronium-like structure in the shallow interface region, it forms the distorted Zundel ion in the deep interface region. In the deep interface region, not only the phosphate oxygen atoms but also the carbonyl oxygen atoms play an important role. More detailed results will be discussed in the poster presentation. (See Fig. 1.)

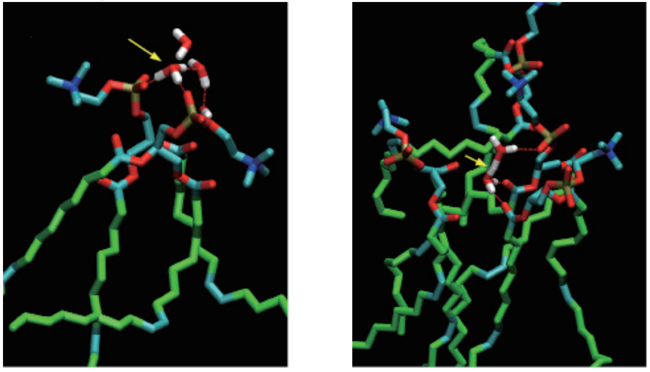

Figure 1: Hydrated excess protons (left) in the shallow DOPC membrane/water interface region and (right) in the deep interface region.

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4PP-64

Effect of Crystal Packing on Protein Conformation and Dynamics

Osamu Miyashita, Ivan Vorontsov, Zak Campbell, Logan Ahlstrom
Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA

Decades of investigation have confirmed the importance of protein dynamics for biological functions. X-ray crystallography has played the major role in structural biology, providing information on protein conformations. However, interpretation of this data is not always trivial. While proteins are flexible and adopt different conformations, X-ray structures represent only a single snapshot of the conformational ensemble. In addition, this static image may be subject to artificial forces such as crystal packing. Some structures may represent conformations that are indeed most stable in solution environment, while some may be unrepresentative of the physiologically relevant forms. It is especially important when several conformations of a protein are available – some conformations reflect their biological context (such as an allosteric effector), whereas others may be under the effect of crystal packing. At present, there is no general guideline for interpreting X-ray structures.

We have been studying several biological systems and examining how experimentally determined structures correlate with the conformational ensembles to provide additional insight to the structural mechanism of their functions. In particular, we established 1) a protocol to perform molecular dynamics simulations of proteins in solution as well as crystalline environment and 2) tools to analyze conformational ensembles using clustering and network analysis. We applied our methods to study the effect of the crystal environment on protein structures at multiple levels: side-chain conformations of cyanovirin-N, mobile loop motions of luciferase, and large-scale domain motions of λ-cro. We showed that, while the conformations of X-ray structures are energetically accessible, they are not always the most energetically favorable conformation. The crystallization processes also may influence the conformational state represented in X-ray data. Thus, the X-ray structure itself is not sufficient to reveal the mechanism of protein function, and could even lead to inaccurate speculations. Our quantitative data from computation should provide useful information on the effect of crystal packing on protein conformation.

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4PP-65

A theoretical analysis on the interaction between Siglec-7 and its ligand by molecular dynamics and *ab initio* FMO method

Kaori Ueno-Noto,[1] Keiko Takano[2]
[1] College of Liberal Arts and Sciences, Kitasato University, Japan
[2] Graduate School of Humanities and Sciences, Ochanomizu University, Japan

Siglecs are a group of receptors in the immunoglobulin superfamily, which specifically recognize glycans that contain sialic acids (Neu5Ac). Siglec-7 belonging to CD33-related Siglecs is mainly expressed on natural killer cell, and draws attentions for its role in the immune system. Attrill *et al.* reported that the ligand binding of Siglec-7 changed by mutations [1]. The mechanism of the ligand recognition, however, has not been elucidated. In order to investigate the specificity of glycan binding of Siglec-7, we analyzed the modulation of the interactions by site-specific mutagenesis.

MP2 level of *ab initio* fragment molecular orbital (FMO) electronic structure calculations (FMO-MP2/6-31G**) [2] were performed with wild-type Siglec-7 as well as seven mutants using the X-ray crystal structure (PDB ID: 2HRL) [1]. The detailed ligand-Siglec interactions were analyzed by Pair Interaction Energy Decomposition Analysis (PIEDA) [2]. We also carried out MD simulations for 9 ns on wild-type and mutants to see dynamical effects caused by mutations.

Figure 1 shows the difference in the ligand-Siglec-7 interaction energy between seven mutants and that of wild type. The experimental results of ligand-binding assay were also depicted [1]. We found a large decrease in the interaction energies in R124A, K131A, N131A, and K135A mutants. These large decreases were predominantly the reduction in electrostatic energy. The decline in W74F due to the reduction in dispersion interaction was also found. These results agree well with the experimental results. On the other hand, we found discrepancies in W85A and dW74F/W85A mutants. Figure 2 shows structural RMSD change of wild-type as well as W85A, dW74F/W85A and R124A mutants obtained by MD simulations. We found the mutagenesis at W85 position significantly destabilized the protein structure.

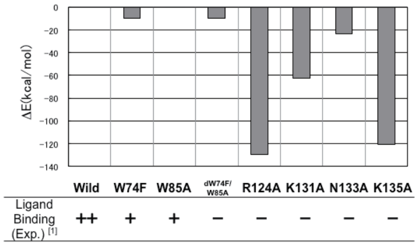

Figure 1. Interaction energies between the ligand and the mutants of Siglec-7 calculated with FMO-MP2/6-31G**

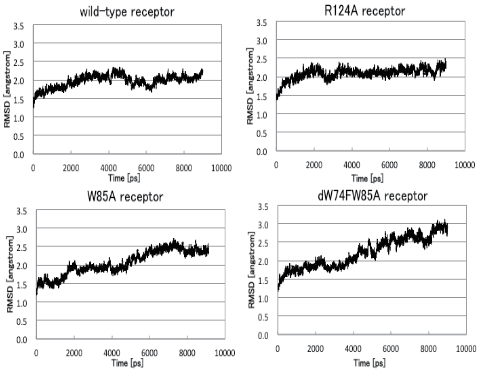

Figure 2. The RMSD of Siglec-7 atoms with respect to the crystal structure (PDB ID;2HRL)

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4PP-66

Electron transfer from cytochrome f to plastocyanin

Tatsuya Joutsuka,[1] Hirotaka Nishioka,[1] Koji Ando[1]
[1] *Department of Chemistry, Graduate School of Science, Kyoto University, Japan*

In photosynthesis, plastocyanin (Pc) shuttles an electron from cytochrome *f* (C*f*) to P700$^+$. Pc is a small, soluble cupredoxin whose ligand structure around the copper ion is distorted trigonal and consists of a cystein (Cys), two histidine (His), and a methionine (Met) residues as shown in Figure 1. C*f* is an N-terminal soluble subunit of cytochrome b_6f that is anchored to the membrane complex by C-terminal helix. Its soluble domain is an atypical *c*-type cytochrome because both its β-sheet secondary structure and the unusual heme axial coordination with the N-terminal amino acid Tyr acting as an axial ligand (Figure 1).

The structures of Pc observed by X-ray crystallography were very similar between the reduced and the oxidized states, in contrast to those in typical inorganic compounds where Cu(I) and Cu(II) tend toward tetrahedral and tetragonal geometries, respectively. The small change indicates that the active site reduces the reorganization energy and thereby accelerates the electron transfer (ET). Hence, the position dependence of the residues around the active site on the reorganization energy can clarify their roles in ET.[1]

For example, when an electron flows from C*f* to Pc, they form a transient complex (Pc/C*f*) which is the transition state (TS) of ET. The His residue is very close to the Tyr residue in the transient complex. This indicates that the His residue, in particular the solvent exposed one, may be crucial to elucidate the ET mechanism.

Accordingly, the purpose of this presentation is to analyze the ET mechanism of the complex Pc/C*f* by *ab initio* quantum chemistry methods.[2] Our focus is on the roles of the residues in the active site of Pc to relate to our previous study.[1]

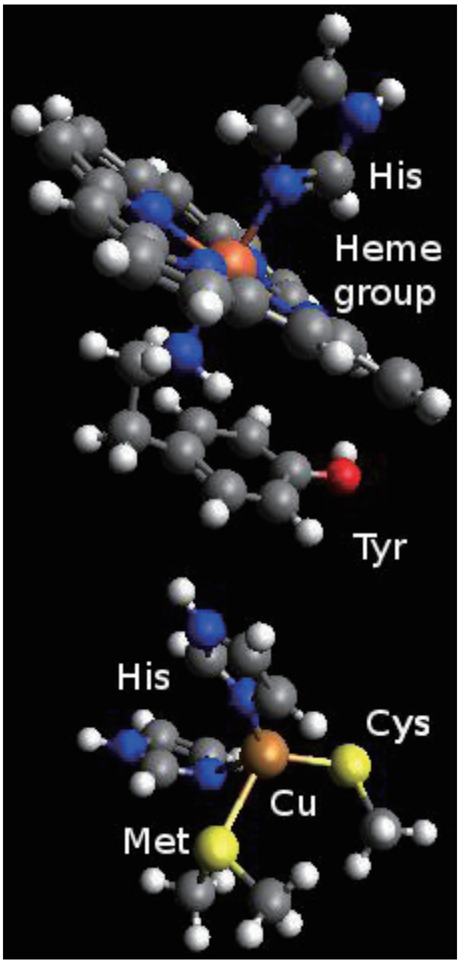

Figure 1. Active site structure of the complex between Pc and C*f*.

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4PP-67

Structural properties and imino proton acidity of silver containing 5-substituted uracils

Toru Matsui[1, 2], Hideaki Miyachi[3], Yasuteru Shigeta[1]

[1]*Department of Material Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka 560-8531, Japan.*
[2] *Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka 560-0043, Japan.*
[3] *School of Medicine, Chiba University, 1-8-1 Inohana, Chuo-ku, Chiba 260-8670, Japan.*

Deoxyribonucleic acid (DNA) contains genetic instructions used in the development and functioning of living organisms. Chemists' interest in DNA has recently been focused on its flexible functioning in living organisms. One of the promising approaches to modify its properties is to coordinate metal ions to nucleobases, nucleosides or nucleotides to form metal-complexed DNA. If metal ions, which have various electronic states, are captured in DNA duplex and controlled to systematically array, one can obtain a hybrid material with multi-functions in mesoscopic scale. These days, many researchers have developed such metal-DNA systems. An example of metal-DNA systems is the formation of [**N**-Ag_2-**N**] (**N**: 5-substituted uracil) bridge by substituting the C5 ligand (X) of deoxyuracil nucleo-oligomer. [**N**-Ag_2-**N**] can be formed even in low pH in the case of **CN** (X=CN), while **T** (X=CH_3) does not seem to capture any silver ion.

We focused on [**N**-Ag_2-**N**] bridges and showed following three points by using B3LYP/aug-cc-pVDZ + pseudo potential (PP) and 6-31++G(d, p) level of theory: (1) The replacement of an imino-proton with Ag(I) increases the stability of the whole duplex in nucleo-oligomer. (2) Four conformations of [**N**-Ag_2-**N**] bridge and two of them (depicted in Figure) are almost degenerate from the view of potential energy. (3) The energy barriers among three structures are no more than 6 kcal/mol. Thus, these structures may fluctuate at room temperature. These results indicated that the replacement of imino-proton with Ag(I) plays a key role in forming [**N**-Ag_2-**N**] bridges. In the poster presentation, we will also introduce a new computational method to provide a pK_a value of an imino-proton in silver mediated **N** and propose a scheme for the formation reaction of silver-mediated base pair [**N**-Ag_2-**N**] from two **N** with two silver ions.

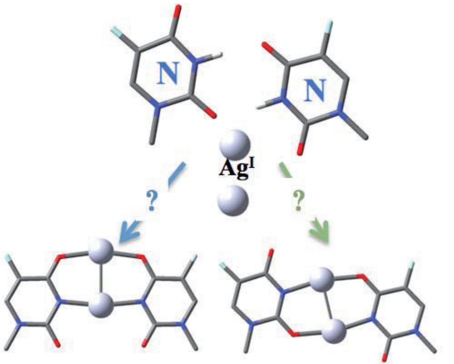

Figure: Possible conformers for the structure of [**N**-Ag_2-**N**] bridge.

4PP-68

Electronic coupling calculation and pathway analysis of electron transfer reaction by using ab initio fragment-based method

Hirotaka Nishioka,[1] Koji Ando[1]
[1]*Graduate School of Science, Kyoto University, Japan*

I. Introduction

Electron transfer (ET) reactions, playing important roles in the biological energy conversion such as photosynthesis and respiration, take place via the electron tunneling between redox centers separated by more than several Å where the tunneling electron uses the electronic states of the protein media as its virtual intermediate states. Therefore, the electronic coupling factor T_{DA}, regulating the biological ET rate, strongly depends on the electronic states of intervening protein. Accurate estimation of T_{DA} requires ab initio quantum chemical methods[1] whose applications, however, have been limited owing to their huge computational cost. To overcome the difficulty, we propose a novel approach to calculate T_{DA} and analyze the tunneling pathway by using the ab initio fragment-based electronic structure methods.

II. FMO-LCMO approach

The FMO-LCMO method, developed by Tsuneyuki *et al.*[2], produces one-electron Hamiltonian of whole system using the output of the fragment molecular orbital (FMO) calculation with computational cost much lower than conventional all-electron calculations. Diagonalizing the FMO–LCMO Hamiltonian matrix, the molecular orbitals (MOs) of the whole system can be described by the linear combination of MOs of the fragments. In our approach[3], T_{DA} is calculated from the energy splitting of the frontier MOs of whole system or perturbation method in terms of the FMO-LCMO Hamiltonian matrix. The tunneling pathway at fragment-based resolution is obtained from the tunneling current method. Moreover, taking into account only the valence MOs of the fragments, we can considerably reduce computational cost to evaluate T_{DA}. We have succeeded in applying our approach to several ET systems.[3]

III. Divide-and-Conquer approach with Natural Bond Orbital Analysis

The Divide-and-Conquer (DC)[4,5] and FMO-MO[6] methods produce the approximated total density matrix of the system. For model protein ET systems, we have analyzed the tunneling pathways in terms of localized MOs such as natural bond orbitals (NBOs) obtained from the DC or FMO-MO density matrix.

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4PP-69

Application of DC-MP2 method to investigate the interaction energy of MK4965 in HIV-1 RT binding pockets

Patchreenart Saparpakorn,[1,2] Masato Kobayashi,[1,3] Hiromi Nakai[1,4,5]
[1]*School of Advanced Science and Engineering, Waseda University, Japan*
[2]*Department of Chemistry, Faculty of Science, Kasetsart University, Thailand*
[3]*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Japan*
[4]*Research Institute for Science and Engineering, Waseda University, Japan*
[5]*CREST, Japan Science and Technology Agency, Japan*

I. Introduction

The reverse transcriptase (RT) of HIV-1 is an essential enzyme converting the single-stranded viral RNA genome into double-stranded proviral DNA prior to its integration into the host genomic DNA. MK4965, a novel NNRTI, reveals high levels of potency against wild-type and some important HIV-1 RT mutants.

II. Methodology

DC-MP2 method [1,2] with 6-31G** basis set using GAMESS program is applied to study the total interaction energies of MK4965 in WT and Y181C HIV-1 RTs. Efficiency of the DC-MP2 method with the effects of SCF buffer radius and correlation buffer radius is validated by comparing the energies and CPU times with those obtained by the conventional MP2 method. The energy distribution of each subsystem of MK4965 and amino acid is also examined.

III. Results and Discussion

Based on the accuracy and CPU times, 6.0 Å of SCF buffer radius and 5.0 Å of correlation buffer radius are appropriate parameters for this study. The deviation of the interaction energies are less than 0.5 kcal/mol for MP2 and SCS-MP2 energies. The main energy distribution is caused by the interaction with Lys102 and chlrobenzonitrile ring subsystems. In addition, the other important energy distributions are from subsystems of Leu100, Lys103, Val106, Tyr188, Phe227, and Leu234. Study of each subsystem of MK4965 reveals that pyrazolopyridine ring causes the main energy distribution to Lys102. In this study, DC-method reveals the efficiency to investigate in the biological system with the less computing time and high accuracy of the calculations. In addition, the results obtained by the DC-method are able to explain the energy distribution in the binding of MK4965 and guide for the drug design.

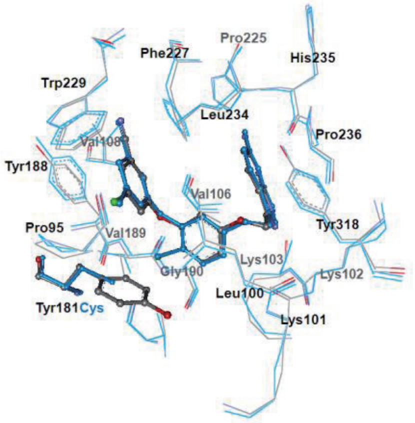

Figure 1. Binding pockets of MK4965

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4PP-70

Binding free energy of oxidized Azurin – reduced Cytochrome c551 Complex

Hiroaki Saito,[1] Masashi Iwayama,[1] Taku Mizukami,[2] Hidemi Nagao[1]
[1]*Faculty of Mathematics and Physics, Institute of Science and Engineering, Kanazawa University, Kanazawa 920-1192 Japan*
[2]*Department of Materials Sciences, Japan Advanced Institute of Science and Technology*

Protein complexes have much interest in the mechanism of catalysis, photosynthesis and physiology in vivo. For instance, the formation of metalloporoteins complex occurs the electron transfer between active site of the proteins, yielding the redox reaction in the protein complex. The synthesis and hydrolytic cleavage of adenosine triphosphate (ATP) are important catalytic reactions concerning metabolism of material and energy in vivo, and those are cased by binding to the protein complex. Also, in the protein-ligand complex, the bound ligand functions as inactivator and changes the dynamical structure correlating the protein functions. Thus, understanding of the binding characters of protein complexes should be a key subject to reveal the biological function of protein system.

Azurin and Cytchrome c551 from Pseudomonas aeruginosa are metalloporoteins, and the bound Az-Cyt protein complex shows the electron transfer between the active sites in vivo. However, since this complex is not accessible to crystallographic investigation, its docking structure in solution is not still known. We have carried out the docking and MD simulations of the protein complex consist of the reduced Azurin (Azred) and oxidized Cytchrome c551 (Cytox) to reveal the structure and dynamics of the system. In these studies, we have shown the stability of the Azred-Cytox complex and the dynamical correlations between residues.

In this study, to evaluate the binding energy of the AZ/C551 complex, at first, we present a possible AZ/C551 complex structure in water solvent by docking AZ and C551 proteins and carry out the MD simulation of AZ/C551 complex in water solvent. From the coordinates in equilibrated state, we calculate the free energy of AZ/C551 complex by estimating the internal energies and the excess chemical potential. The binding free energies are evaluated by the difference of free energy of protein complex and those of monomer proteins. The variation of protein structures and binding free energy are also discussed in this study.

4PP-71

Towards making periodic table of motifs in irreducible decomposition of protein folding

Masanori Yamanaka,[1]
[1]*Department of Physics, College of Science and Technology, Nihon University, Japan*

I. Introduction

The classification of protein tertiary structures is one of the central issues of molecular biology. CATH [1], FSSP [2], and SCOP [3] are well-known databases which provide structural classifications of proteins.

The genus, or Euler characteristic, is the most fundamental topological invariant in mathematics. The classification of biopolymers with respect to the topological invariant has been extensively studied. One such example is the classification of ring-shaped DNA [4]. Classification of RNA folding by the use of pseudo-knots is another example [5]. The genus is calculated and is assigned to an RNA as the classification index. The scaled Gauss metric is introduced to construct a measure of similarity of protein shapes [6]. Recently, the *fatgraph* model has been proposed to classify proteins [7]. A set of topological invariants is constructed to characterize the protein structure. These programs are beautifully demonstrated to classify the protein domains in the CATH database.

II. Method and results

In our method, the structure of protein is simplified by a graph composed of the backbone and the hydrogen bond network and is embedded into the surface of the two dimensional torus. This procedure is a standard embedding in topological combinatorics. The genus of the torus is used to classify the protein tertiary structure. We classify the motifs of protein by the irreducible decomposition with respect to the genus. We use the genus of the motif as a classification index, which corresponds to the atomic number in the periodic table of the elements. To assign the functions of motifs to the genus, i.e. a kind of the atomic number, we analyze the correspondence between motif and ligand. We search all motifs with the ligand, classify the motifs with respect to the genus, and make a table of the appearance frequency of the genus. We find that some ligands have correlation with the genus. This attempt may open a periodic table of motifs of protein.

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4PP-72

Effect of Multivalent Ion on Attractive Interaction between Like-Charged Macromolecules Immersed in an Electrolyte Solution

Ryo Akiyama,[1] Ryo Sakata,[1] Yoji Kubota[1,]
[1]*Department of Chemistry, Kyushu University, Japan*

I. Introduction

In dilute electrolyte solution two like-charged macroions are repel each other. The effective interaction is screened Coulomb interaction. However, the effective interaction often becomes attractive in a bio-fluid. For example, G-actins make a strong polymer and bundle structures in biological condition, although they are negatively charged proteins. Another example is DNA, which is negatively charged long polymer. In dilute electrolyte, it is stretched. When the electrolyte concentration becomes higher, the polymer collapses. It means that the like-charged parts of polymer are effectively attracted each other. However, the attraction disappears as the concentration increases. The coil-globule transition is important in reading genetic information of DNA. Therefore, this reentrant behavior is not only interest in chemical context, but also important in biological context.

II. Theory and Model

The OZ-HNC theory was adopted in this study, because it was useful method in this problem [1]. The equations were solved numerically. The details of the calculations have been described in earlier publications [2]. Neutral hard spheres (the diameter is 2.8A) were adopted as the solvent molecules. This size is the effective size of water molecule. The ions were modeled as charged hard spheres whose diameter was also 2.8A. Each anion and each cation had charge −e and e, respectively. The macroions were also modeled as charged hard spheres. The diameter of macroion was set at 16.8A and. The Coulomb potential was divided by 78.5, the dielectric constant of water.

II. Results

The effective interaction between two like-charged macromolecules were obtained. The results showed the reentrant behavior. The attraction was explained by using the idea of classical "covalent bond". The "bond" was analyzed by the Kirkwood super position approximation. There was a good agreement between the stability of macroion dimer and the local density between the macroions. It means that there is an analogy between it and the linear combination of atomic orbital (LCAO) approximation for chemical bonds.

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4PP-73

Fragment molecular orbital study for interaction between influenza virus neuraminidase and antiviral drug

Kaori Fukuzawa,[1,2] Yuji Mochizuki,[2,3] Hiroki Mibe,[3] Chiduru Watanabe[2], Shigenori Tanaka[4], Tatsuya Nakano[2,5]

[1] *Mizuho Information & Research Institute Inc., 2-3 Kanda Nishiki-Cho, Chiyoda-ku, Tokyo 101-8443, Japan*

[2] *Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan*

[3] *Department of Chemistry and Research Center for Smart Molecules, Faculty of Science, Rikkyo University, 3-34-1 Nishi-ikebukuro, Toshima-ku, Tokyo 171-8501, Japan*

[4] *Graduate School of System Informatics, Department of Computational Science, Kobe University, 1-1, Rokkodai, Nada, Kobe 657-8501, Japan*

[5] *Division of Medicinal Safety Science, National Institute of Health Sciences, 1-18-1 Kamiyoga, Setagaya-ku, Tokyo 158-8501, Japan*

Ab initio electronic structure calculations for interaction between influenza viral surface proteins, neuraminidase (NA), and antiviral drug, oseltamivir (Tamiflu) and zanamivir (Relenza), have been performed on the basis of the fragment molecular orbital (FMO) method. The NA monomer (386 amino acid residues, 5749 atoms) complexed with inhibitor agents were calculated at the FMO-MP2/6-31G level. The inter-fragment interaction energy (IFIE) analysis was performed to reveal the interactions between inhibitor and its binding pocket. Hydrogen bond network structures of interactions among the inhibitor and surrounding amino acid residues were characterized, and difference of binding mechanism between two inhibitors was examined. Such theoretical analyses could be helpful to develop the effective inhibitor agent against the drug resistant mutant.

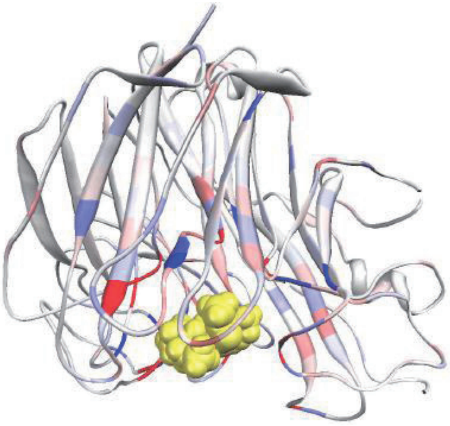

Fig. IFIE between oseltamivir (yellow) and each amino acid residue. Attractive and repulsive interactions are colored by red and blue, respectively.

Acknowledgement

This work was supported by the RISS project at the institute of Industrial Science (IIS) of the University of Tokyo and the SFR project at Rikkyo University.

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4PP-74

Energetical validation of the cleft open-close and the lever-arm swing of molecular motor myosin

Jun Ohnuki, Takato Sato and Mitsunori Takano
Dept Pure & Appl Phys, Grad Scl Adv Sci & Eng, Waseda Univ

Muscle contraction arises from a unidirectional motion of myosin along an actin filament. It is widely believed that the two large structural changes of myosin, coupled with the chemical state of the nucleotide in the catalytic site of myosin, drive the unidirectional movement: the open-close of the actin-binding cleft regulates the binding to the actin filament, and the swing of the lever-arm (the so-called “power stroke”) generates the force. However, this widely-held mechanism relies largely on the structural studies, and accompanying energetics in aqueous solution remains elusive. Therefore, we here validate, from the energetical viewpoint, the possibility of those nucleotide-induced structural changes. To this end, we investigate the free energy landscapes along the reaction coordinates representing the cleft open-close and the lever-arm swing by using the replica exchange umbrella sampling method, which is one of the powerful conformational sampling methods. We found that the most stable state of the cleft changes depending on the bound nucleotide, which is in agreement with the previous studies. On the other hand, the power stroke of the lever-arm was found to be unfavorable even in the nucleotide-free state. However, free-energy differences for both structural changes were not so large, allowing large thermal fluctuations at room temperature. We then decompose the potential energies on the residue-residue basis to identify the key residues. We finally address the mutual relation between the actin-binding cleft and the lever-arm motions.

4PP-75

Orbital Views of Molecular Conductance Perturbed by Anchor Units

Yuta Tsuji,[1] Aleksandar Staykov,[1] Kazunari Yoshizawa[1]
[1] *Institute for Materials Chemistry and Engineering and International Research Center for Molecular Systems, Kyushu University, Japan*

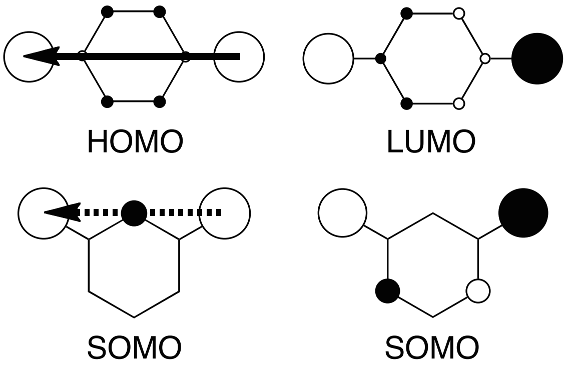

Figure1. Frontier orbitals of *p*-BDT and *m*-BDT, symmetry-allowed (solid arrow), and symmetry-forbidden (dashed arrow) routes for electron transport.

During the last two decades studies of single-molecular electronic devices have gained great attention of the nanoscale science and technology. The variety of potential applications of molecular devices such as switches, rectifiers, and memories requires detailed understanding of the electron transport properties through a single molecule. Site-specific electron transport phenomena through benzene and benzenedithiol (BDT) derivatives are discussed on the basis of a qualitative Hückel molecular orbital analysis for better understanding of the effect of anchoring sulfur atoms. A recent work [1,2] for the orbital control of electron transport through aromatic hydrocarbons provided an important concept for the design of high-conductance connections of molecule with anchoring atoms. In this work the origin of the frontier orbitals of BDT derivatives, the effect of the sulfur atoms on the orbitals and on the electron transport properties, and the applicability of the theoretical concept on aromatic hydrocarbons with the anchoring units are studied. The results demonstrate that the orbital view predictions are applicable to molecules perturbed by the anchoring units. The electron transport properties of benzene are found to be qualitatively consistent with those of BDT with respect to the site dependence. To verify the result of the Hückel molecular orbital calculations, fragment molecular orbital analyses with the extended Hückel molecular orbital theory and electron transport calculations with density functional theory are performed. Calculated results are in good agreement with the orbital interaction analysis. The phase, amplitude, and spatial distribution of the frontier orbitals play an essential role in the design of the electron transport properties through aromatic hydrocarbons [3].

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4PP-76

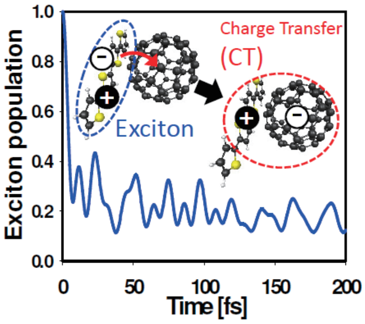
Quantum dynamics for organic solar cells

Hiroyuki Tamura,[1] Irene Burghardt,[2] Masaru Tsukada [1]
[1] *WPI-Advanced Institute for Material Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan*
[2] *Institute of Physical and Theoretical Chemistry,Goethe University Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany*

Organic solar cells typically consisting of conjugated polymers and fullerenes are one of promising next-generation photovoltaics owing to their potential for cost-effective energy sources, so that great efforts have been devoted to the development of high-efficiency organic solar cells. The energy conversion efficiency of organic solar cells would be determined by several processes, including photoabsorption (exciton generation), exciton diffusion in the donor material, exciton dissociation (charge transfer) at the donor-acceptor heterojunction, and transports of free electron and hole to the electrodes. Understanding these mechanisms at microscopic level is important to provide design rules for high-efficiency photovoltaics.

Here, we investigate the exciton dissociations at oligothiophene/C_{60} donor-acceptor heterojunctions [1]. The non-perturbative charge transfer is analyzed based on quantum dynamics calculations in a diabatic representation considering the vibronic coupling. Our quasi-diabatization scheme [1] is convenient for analyzing photovoltaic processes, and can be applied for any *ab initio* and DFT methods. The electronic structure and the vibronic coupling are calculated by using the long-range corrected TDDFT [2]. We take advantage of the hierarchical electron phonon (HEP) model [1,3] for systematic renormalizations of the vibronic coupling of large systems. We have proven that the truncated HEP Hamiltonian can exactly reproduce short-time dynamics of large systems. The quantum dynamics calculations are performed by using the multi-configuration time-dependent Hartree (MCTDH) method [4].

Our quantum dynamics calculations exhibit ultrafast exciton dissociations owing to the strong coupling between the exciton and charge transfer states, as observed in the time-resolved spectroscopies. The intra-molecular high-frequency vibrational modes are found to dominate the ultrafast dynamics. The coupling strength and relative energy between the exciton and charge transfer states depend sensitively on the stacking structure of thiophene and C_{60}, which in turn affects the absorption spectra and the dynamics of exciton dissociations [1].



Time-evolution of the exciton population at the oligothiophene/C_{60} heterojunction

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4PP-77

Determination of Local Chirality of Irregular Single-Walled Carbon Nanotube Based on Individual Hexagons

Joonghan Kim and Keiji Morokuma
Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

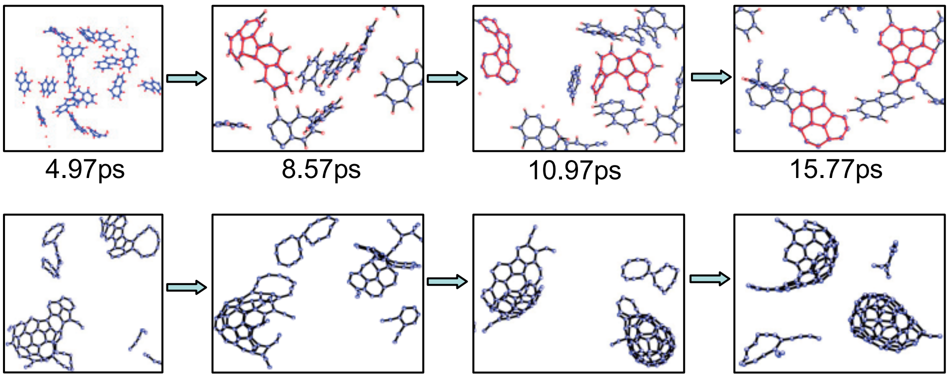
The chirality of single-walled carbon nanotubes (SWCNTs) has a great importance since their physical and electronic properties strongly depend on the chirality. However, the chirality of irregular structures of SWCNT, for instance those formed during growth of SWCNT, was difficult to define. Therefore, we have developed a powerful theoretical method for the determination of the local chirality based on individual hexagons that compose SWCNT. The new method and code have been applied to various SWCNT-like irregular structures that are formed during molecular dynamics simulation of the growth process. The local chiral angles and their distributions are well defined and easily calculated for irregular structures as well as ideal structures of SWCNT. This tool could aid the further investigation of the chirality-controlled SWCNT growth.

4PP-78

Fullerene formation from hydrocarbon combustions: Quantum chemical molecular dynamics study

Hai-Bei Li,[1] Stephan Irle,[2] Keiji Morokuma[1,3]
[1]*Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan*
[2]*Institute for Advanced Research and Department of Chemistry, Nagoya University, Nagoya, Japan*
[3]*Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA, USA*

Combustion of hydrocarbon fuels in lean oxygen flame offers advantages for large-scale fullerene production [1]. Saha *et al.* [2] performed high temperature simulations of benzene combustion by gradually reducing hydrogen atoms randomly using density-functional tight-binding (DFTB)-based quantum chemical molecular dynamics (QM/MD). In this work, we simulate fullerene formation from naphthalene combustion at 1500 K and 2500 K. All QM/MD simulations were performed by employing a Nose Hoover chain thermostat, and carbon densities of 0.119 and 0.026 g/cm^3, respectively. A Monte Carlo-based hydrogen removal strategy was devised where we calculate the probability factor for each candidate structure after removing two hydrogen atoms in randomly selected positions, and select the candidate hydrogen pair randomly under consideration of Boltzmann weights for the environmental temperature. One hydrogen pair is removed every 0.235 ps and 0.470 ps at 1500 K and 2500 K, respectively, until all hydrogen is removed from the system. One selected trajectory is shown in the figure below. Although the mechanism of fullerene formation is similar to previous results [2], in our simulation, lower carbon density and lower temperature favor the formation of smaller size fullerenes. Our new hydrogen removal scheme tends to produce more cage structures than the random removal scheme of [2].



4.97ps 8.57ps 10.97ps 15.77ps

20.09ps 25.30ps 40.20ps 65.04ps

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4PP-79

First-principles Study of STM-induced Melamine/Cu(001) Switch; Energy Barrier Change with Bias and Various tip positions

Tatsuhiko Ohto,[1,2] Ivan Rungger[2], Koichi Yamashita,[1] Stefano Sanvito[2]
and Hisao Nakamura[3]
[1]*Department of Chemical System Engineering, The University of Tokyo, Japan*
[2]*School of Physics, Trinity College Dublin and CRANN, Ireland*
[3]*Nanosystem Research Institute(NRI), RICS, AIST, Japan*

I. Introduction

The manipulation or stimulation of molecules using Scanning Tunneling Microscopy (STM) is highly promising. Pan et al [1] found a STM-induced melamine/Cu(001) switch (C1 to C2, Figure1) and analyzed its mechanism by a typical model. Such a model uses *ad hoc* parameters and the switching mechanism is not fully understood. The validation of them using first-principles calculations is required.

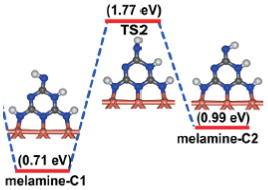

Figure 1. Structures of melamine/Cu(001) system.[1]

II. Method

Current-induced forces are calculated by SMEAGOL program code [2], which is based on the nonequilibrium Green's function method with density functional theory. The explicit evaluation of the current-induced forces enables us to obtain stable structures under arbital STM-tip configurations with a finite bias. The nudged elastic band (NEB) method was implemented into SMEAGOL to obtain minimum energy path (MEP) between C1 and C2 structures. Because the total energy of open systems is not well-defined, we calculated the potential energy by integrating forces along MEP.

III. Results

The energy landscape calculated at zero bias was almost the same with that of Ref. 1. The energy barrier change was 0.06 eV within ±1.0 V, which is attributed to the dipole-filed interaction (no electron-wind force). Therefore, this barrier change can be reproduced by the calculation of a free molecule in electric field. (Figure 2) When the distance between the tip and the molecule is close, the barrier change becomes large but these configurations destroy the basic energy landscape. However, the barrier change of 0.06 eV is 1/4 smaller than the assumption in Ref. 1. The analysis of the switching mechanism by a master equation using first principles results will be presented.

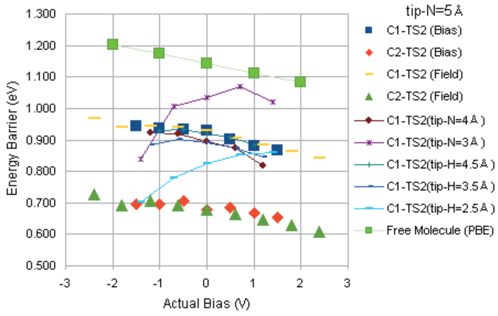

Figure 2. Comparison of the energy barrier with finite bias

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[2] Rocha A *et al.* PRB**73**(2006)085414, Zhang R *et al.* submitted

4PP-80

Functional Features of Voids of Nanosized Golden Fullerenes

Eugene S. Kryachko
Bogolyubov Institute for Theoretical Physics, Kiev, 03680 Ukraine
E-mail: eugene.kryachko@ulg.ac.be

Generally speaking, an arbitrary 3D molecular structure is either space-filled, compact, without any void, or possesses some void(s) or emptiness that result in a hollow cage shape. Fullerenes, such as the buckyball C_{60}, belong to the latter category. Similar fullerene-like structures or hollow cages have been recently discovered for other chemical elements, among which gold is a particular one – definitely, 'noblesse oblige' works out – due to its rather unique properties mostly dictated by strong relativistic effects.

When one molecule interacts with another, their outer space between them is patterned by chemical bonds. In this sense, hollow molecular cages are distinguishably different. If a void of an arbitrary fullerene is of a sufficient size, it enables to form chemical bond(s) in the interior, void space with guest atoms, ions or molecules which are trapped inside, encapsulated or confined within void. This results in the formation of so called 'endohedral' or @-fullerenes which are manifest in a variety of remarkable features. Therefore, by the definition, molecular hollow cages possess atoms that are capable, on the one hand, to form chemical bonds with molecules from the outer space and on the other, from the inner, void one. This implies a bifunctionality of the chemical reactivity of such molecular systems - the outer or exo-reactivity, on the one hand, and the inner, void, or endo-reactivity on the other.

The present work further pursues the theme of the void molecular reactivity [1,2] and investigates the functional features of void reactivity of nanosized golden fullerenes Au_{32} and higher by invoking, instead of the global characteristics, such as the ionization energy and electron affinity, which traditionally characterize chemical reactivity, the local ones: the molecular electrostatic potential, HOMO-LUMO patterns, and atomic and ionic probing species. The formation of the chemical bonding patters are studied for some encaged atoms and diatoms, and compared with the analogous endohedral C_{60}-fullerenes. A surprising confinement propensity of the 3D space-filled cluster $Au_{20}(T_d)$ is under consideration as well.

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4PP-81

Theoretical investigation of charge-transport properties in organic single crystals from constrained density functional theory

Shotaro Watanabe, Kenji Morihashi
Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan

I. Introduction

The charge-transfer rate in electron and hole transfer is one of important factors that show transport properties of electronic materials. Therefore, a reliable method to compute charge-transfer rate in electronic materials would contribute much to the development of electronic devices. The computational methods of charge-transfer rate have been developed on the basis of Marcus theory, and *ab initio* method and density functional theory (DFT) have been used to calculate Marcus parameters. In this work, we used constrained density functional theory (CDFT) [1] to calculate these parameters and estimated intermolecular charge-transfer rates in organic single crystals, naphthalene and anthracene.

II. Calculations and Results

The intermolecular charge-transfer rate, k_{CT}, can be written as [2]

$$k_{CT} = \frac{2\pi}{\hbar}\left|V_{if}\right|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-\left(\Delta G^0_{CT} - \lambda\right)^2}{4\lambda k_B T}\right)$$

where V_{if} is the electronic coupling matrix element between the initial and final states, λ is the reorganization energy, and ΔG^0_{CT} is the change in Gibbs free energy from initial to final state. Using these parameters obtained from CDFT calculations, we calculated intermolecular charge-transfer rates shown in Figure1. The hole transport properties of naphthalene crystal are compiled in Table 1.

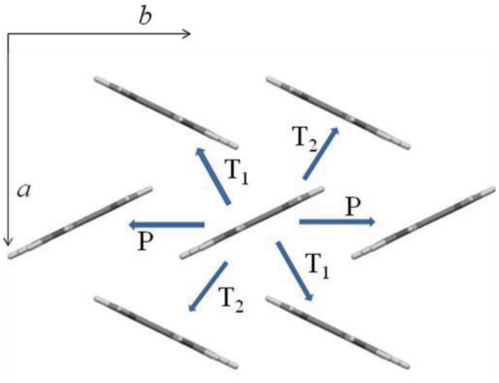

Figure 1. Crystal structure of organic single crystal.

Table 1. Marcus parameters.

	V_{if} [eV]	λ [eV]	ΔG^0_{HT} [eV]	k_{HT} [s^{-1}]
T_1	0.05799	0.1826	-0.1732	1.312×10^{14}
T_2	0.03278	0.1865	0.1732	5.068×10^{10}
P	0.06058	0.1845	0	2.401×10^{13}

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4PP-82

Catalytic activity of gold clusters on the “inert” h-BN surface

Min Gao, Andrey Lyalin, Tetsuya Taketsugu
Graduate School of Science, Hokkaido University, Japan

The unique catalytic activity of gold nanoparticles in oxidation reactions by molecular oxygen was discovered experimentally more than 20 years ago [1]. It was shown that the so-called "active" supports, such as metal oxides, considerably influencing the catalytic activity of the supported gold clusters [2, 3]. Recently, it has been demonstrated experimentally, that small gold clusters deposited on “insert” h-BN support are efficient and robust catalysts [4]. However origin of the catalytic activity of gold clusters supported on h-BN has yet to be fully understood. The present work aimed to clarify whether the catalytic activity of Au_n/h-BN is the intrinsic property of gold clusters or not.

In the present work the structural and electronic properties of Au and Au_2 adsorbed on the regular h-BN surface, as well as on the impurity and vacancy defects on the h-BN surface have been studied theoretically using DFT at the GGA level with the Wu-Chen functional. The most stable geometry structures, surface relaxations, adsorption energies and charge transfers from the h-BN surface to Au and Au_2 are investigated with the aim to understand the specific role played by the support in formation of the catalytic properties of gold. In order to model the catalytic activity of gold clusters supported on h-BN surface we studied adsorption and activation of oxygen molecule on Au/h-BN and Au_2/h-BN. We demonstrate that catalytic activity of gold clusters can be sensitive not only to the interaction with the active support materials, such as metal oxides, but also to the interaction with the inert supports, such as h-BN. It is shown that vacancy and impurity defects on h-BN surface can promote the catalytic activity of the supported Au clusters and enhance the activation of the adsorbed O_2. The charge transfer from the support to the gold clusters plays an important role in formation of their catalytic properties [4, 5].

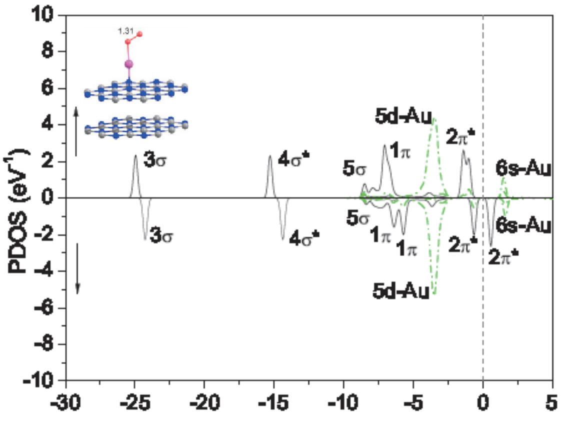

Figure 1. PDOS projected on the O_2 supported on h-BN/Au (solid line) and Au atom (dashed line)

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4PP-83

QM/MD Simulations of Graphene Hydrogenation

Ying Wang, Hu-Jun Qian, Stephan Irle

Institute for Advanced Research and Department of Chemistry, Nagoya University, 464-8601 Nagoya, Japan

Chemical adsorption of hydrogen atoms on graphite surfaces has attracted considerable interest due to its relevance for a broad range of areas including plasma/fusion physics, gap tuning in graphene, and hydrogen storage. We computed counterpoise-corrected DFT, ROMP2, ROCCSD, and ROCCSD(T) potential energy curves (PECs) based on relaxed-scan UB3LYP/cc-pVDZ geometries for the approach of atomic hydrogen head-on to a carbon atom of an inner hexagon of pyrene C16H10 and coronene C24H12. Such attack leads to the only global potential energy minimum corresponding to chemisorbed H (relative energy for CCSD(T) around -0.4 eV), and a barrier (CCSD(T): 0.5 eV) for the H approach. Interestingly, ROCCSD(T)//UB3LYP PECs are close to that of pure UB3LYP.

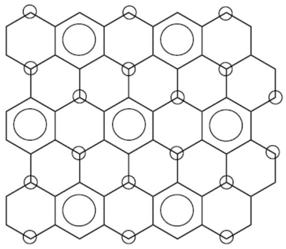

Figure 1. All-para hydrogenated graphene corresponding to 25% coverage as observed in experiment [1] and during our QM/MD simulations.

We then modified the C-H parameter set for the spin-polarized self-consistent-charge density-functional tight-binding (sSCC-DFTB) method to reproduce the CCSD(T)-based PEC at a tiny fraction of the computational cost. Using this quantum chemical potential, we performed direct Born-Oppenheimer MD simulations while "shooting" H atoms in 0.5 ps intervals with incident velocity of 0.4 eV aimed at a periodic graphite target with randomly selected spin. The simulations were carried out at a constant temperature of 300 K. Chemisorption may occur in principle in random positions on the graphite with little preference for the adsorption site, causing H-frustrated adsorption patterns over time [1] as reported by Flores et al. [2]. However, during prolong exposure to H bombardment, a para-adsorption pattern (see Figure 1), proposed previously by Boukhvalov et al. [3], emerges as a consequence of repeated surface reorganization due to associative H2 elimination [1].

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4PP-84

Finite length Armchair Carbon Nanotubes: HOMO-LUMO gap oscillation and conjugated circuit

Noriyuki Mizoguchi
Meiji Pharmaceutical University, Kiyose, Tokyo 2-522-1, Japan

An interesting aspect of finite-length carbon nanotubes (CNTs) is the quantum finite-size effects of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It has been shown that the HOMO-LUMO gaps in armchair CNTs show the oscillation depending on the number of carbon layers along the tubular length axis. In this paper this oscillation of HOMO-LUMO gaps are discussed in terms of Sachs graphs, conjugated circuits, and Clar structures.

Sachs formula enables us to obtain the coefficients of the characteristic polynomial for a conjugated molecule G. If the constant term $a_N(G)$ is zero, then the molecule's pi-system has non-bonding molecular orbitals. A Sachs graph S_N with all the vertices in G is obtained by the superposition of two Kekule structures for G. Circuits found in Sachs graphs S_N are conjugated circuits for G.

Sachs graphs S_N were studied for $(n,n)_m$ armchair CNT. Here m stands for the number of layers in CNT. Figure 1 shows three Kekule structures and two Sachs graphs for $(2,2)_2$ armchair CNT. Superposition of K_1 and K_2 produces Sachs graphs S_{N1}, which contains two 6-membered conjugated circuits and one 8-membered conjugated circuit. Superposition of K_1 and K_3 produces Sachs graphs S_{N2}, which is Clar formula for $(2,2)_2$ armchair CNT. We found that Sachs graphs S_N for $(n,n)_m$ armchair CNT contain not only 4k+2-membered but also 4k-membered conjugated circuit. Note that benzenoid hydrocarbons can have only 4k + 2 conjugated circuits. By using Sachs formula we found that the constant term a_N for $(n,n)_m$ armchair CNT is zero if m=3j, and non-zero otherwise. Thus it was shown that the oscillation of HOMO-LUMO gaps arises from the existence of 4k-membered conjugated circuits in $(n,n)_m$ armchair CNT. Clar formulae were found in Sachs graphs for $(n,n)_m$ armchair CNT with m=3j+2.

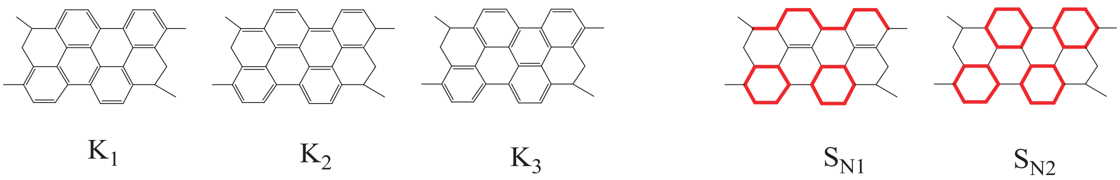
K_1 K_2 K_3 S_{N1} S_{N2}

Fig.1 Three Kekule structures and two Sachs graphs for $(2,2)_2$ armchair CNT

4PP-85

Relativistic quantum chemistry of heavy elements, hadronic atoms and heavy ions collisions

Alexander Glushkov,[1,2]
[1]*Odessa OSENU University, P.O.Box 24a, Odessa-9, 65009, Ukraine*
[2]*ISAN, Russian Academy of Scinces, Troitsk, Moscow reg., 142090, Russia*

The gauge-invariant relativistic many-body perturbation theory approach [1] to consistent calculation of the spectra for heavy and superheavy elements (isotopes) and hadronic atomic systems ions with an account of relativistic, correlation, nuclear, radiative effects is presented. Zeroth approximation is generated by the effective ab initio model functional, constructed on the basis of the comprehensive gauge invariance QED procedure. The wave functions zeroth basis is found from the Klein-Gordon (pion atom) or Dirac (kaon, hyperon) equation. The potential includes the core ab initio potential, the electric and polarization potentials of a nucleus (the Gauss and Fermi models and relativistic Dirac-Kohn-Sham approach for charge distribution in a nucleus are considered). For superheavy ions the correlation corrections of high orders are accounted for within the Green function method. The magnetic inter-electron interaction is accounted for in the lowest order, the Lamb shift polarization part- in the Uhling-Serber approximation and the self-energy part – within the Green functions method. We carried out calculations :1).energy levels, hfs parameters for superheavy Li-like ions for different models of the charge distribution in a nucleus and super heavy atoms Z=114-118; 3). Shifts and widths of transitions (2p-1s,3d-2p, 4f-3d) in the pionic and kaonic atoms (He, U etc.). Further a new consistent unified quantum mechanics and QED approach is developed and applied for description of the heavy ions collisions and heavy quasimolecules. To calculate the collision cross-section and quasi-molecule energy characteristics we use modified versions of the relativistic energy approach, based on the S-matrix Gell-Mann and Low formalism, and operator perturbation theory approach [2]. The nuclear subsystem and electron subsystem has been considered as two parts of the complicated system, interacting with each other through the model potential. The nuclear system dynamics has been treated within the Dirac equation with effective potential. The calculation is carried out for the ^{238}U+^{238}U, ^{232}Th+^{250}Cf and ^{238}U+^{248}Cm systems and diatomics with X^{112} , X^{114} atoms.

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