JST Basic Research Programs

C R E S T

(Core Research for Evolutional Science and Technology)

Annual Report for Research Work in the fiscal year 2008

Research Area :

High Performance Computing for Multi-scale and Multi-physics Phenomena

Research Theme

Realizing super-accurate predictions and giant-molecular designs: breakthrough of frontiers of quantum chemistry with innovative methodologies in computational science

Name of Research Director, Belonging and Title:

Hiroshi Nakatsuji, Quantum Chemistry Research Institute, Director

□Note

The content of this description is published in the HP of the Area, etc. as it is.

You are requested to take full care of the error or omission of a word, and also to prepare the report, taking the necessary security of Intellectual Property etc. into consideration.

10.5 point size of character is to be used.

§1. Outline of Research Work

Quantum principles like the Schrödinger equation govern chemistry, biology and physics of the material science. If this basic equation can be solved, we can accurately predict the phenomena of matter and science. Recently, we have discovered a general method of solving this basic equation analytically. In this project, we will apply this theory to the study of various atoms and molecules, and provide clear understanding for basic phenomena of matter and science. Our SAC/SAC-CI method is well established as a reliable method for studying ground, excited, ionized and electron attached states of diverse fields in science. In this project, this theory will be improved to be more efficient and more accurate method. Based on the SAC-CI method, new strategies will be established for investigating photo-electron processes in biological phenomena, crystals, polymers, proteins, and DNA. In this project, we will study the most of the interested phenomenon of the modern material science from small molecular to giant molecular systems seamlessly with the reliable method.

In this year, the method of the local Schrödinger equation was applied up to 6-electron atoms and molecules and very accurate physical quantities were obtained by the method. The obtained very accurate potential energy curves were confirmed the chemical reactions.

As SAC/SAC-CI science, the primal algorithm of acceleration of the SAC-CI general-R method was developed. The theory and its application program of the magnetic circular dichroism spectrum were developed based on the SAC-CI theory. In the theoretical studies of circular dichroism (CD) spectrum, the relations between sugar-basis conformation and observed spectrum were investigated for the CD spectrum of DNA. This study will initiate a new methodology to predict the helical-conformations of DNAs by theoretical calculation and spectroscopy. A systematic assignment of spectrum was provided for amino acids in the high-energy region. These results provided a fundamental aspect to study the origin of homochirality. Electronic excitation and ionization of inner-shell electron were studied and vibrational structures of spectrum were analyzed. The phosphorescence process was studied for organic electro-luminescence molecules. As application to photobiology, the color-tuning mechanism of human visual cone pigments was studied.

In quantum chemistry of giant molecular systems, the program for giant system was improved using efficient parallel computing methods. The early process of a photo-induced phase transition (PIPT) was studied. Our results suggested the possibility of concerted mechanism in PIPTs.

§2. Content of Research Work

(Nakatsuji Group)

1. Quantum chemistry as an accurate predictive science

Accurately solving the Schrödinger equation should be one of the most important central roles for quantum chemistry and the free iterative complement interaction (Free ICI) method was proposed to realize that. It has been applied to various systems and that availability and very high accuracy have

been not only analytically but also numerically confirmed [3,4,6,10,12,17,19].

Exactness of the solutions of the free ICI method — We have investigated how accurately the free ICI wave function satisfies the Schrödinger equation. Especially, we considered not only the upper bound energy (obtained with the ordinary variation principle) but also the lower bound energy (evaluated with the H-square error) to know the existence region of the true energy. We applied the present procedure to the ground state of helium atom, which has been believed for 80 years that there is no closed solution. From both bounds, we could obtain the correct energy of the ground state of helium atom as **-2.903 724 377 034 119 598 311 159 245 194 4** (a.u.), which is strictly and mathematically guaranteed to be correct up to 32 digits [10,17,19].

Development of the program and accurate calculations for general atoms and molecules — We also have developed the Local Schrödinger Equation (LSE) to solve the Schrödinger equation accurately for general atomic and molecular systems. In the present year, we have especially developed the algorithm and efficient method to be applicable to general atoms and molecules in realistic computational time. We could propose the efficient method for the antisymmetrization problem of the partially correlated wave function to avoid $N!$ permutations, which should be one of the most crucial problems when we apply the LSE method to many electron systems. The Davidson-like diagonalization has also been introduced to solve the large dimensional eigenvalue problem. We applied the present method up to 6-electron systems, Li_2^+, BeH, Li_2, CH^+, and obtained the very accurate solutions not only for the ground states but also for a few low-lying excited states and their potential energy curves. Table I summarizes the results and Fig. 1 shows the accurate potential energy curves of Li_2^+ system. The obtained energies were quite accurate, comparing to the conventional full CI results, and the potential energy curve could be correctly obtained even up to the dissociation limit.

Table I Free ICI LSE calculations of some molecules

Atoms & Molecules	No. Elec.	Order	M_n	Energy (a.u.)	Ref. (a.u.)
Be	4	4	1770	-14.667 300	-14.667 355
LiH	4	4	2645	-8.070 516	-8.070 553
B	5	4	15038	-24.653 872	(-24.653 93)
$Li_2^+(X^2\Sigma_g^+)$	5	4	3386	-14.805 243	(No ref.)
$Li_2^+(A^2\Sigma_g^+)$	5	4	3386	-14.664 371	(No ref.)
$BeH(X^2\Sigma^+)$	5	4	6772	-15.244 176	(No ref.)
$BeH(A^2\Sigma^+)$	5	4	6772	-15.035 362	(No ref.)
$Li_2(X^2\Sigma_g^+)$	6	4	16418	-14.987 596	(No ref.)
$Li_2(A^2\Sigma_g^+)$	6	4	16418	-14.868 342	(No ref.)
BH	6	3	7219	-25.286 413	(No ref.)

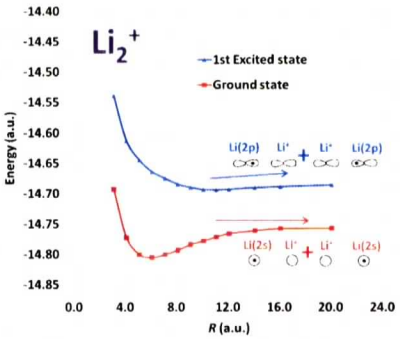

Fig. 1 The potential curves of Li_2^+

2. SAC/SAC-CI science

Highly efficient and fairly accurate algorithm of the SAC-CI method — The direct algorithm is developing in the SAC-CI general-R method for more efficient and accurate calculations and the SAC-CI SD-R method is applied diverse phenomena of chemistry. In this year, the fundamental

program was developed for improving the efficiency of the SAC-CI general-R method. The energy gradient method of the SAC-CI SD-R was applied to the relaxations of porphins in excited states. The SAC-CI calculations well reproduced the observed fluorescence energies and the predicted geometry relaxations in excited states were very small. Our results proposed that this very small relaxation would be essentially important for the excitation energy transfer, which is important process in photosynthesis.

Circular dichroism spectra for a deoxyguanosine; one of the component molecules of DNA — Circular dichroism (CD) spectra are widely used for studying the structures of DNA and RNA in solution. Experimental observations show that the CD spectrum of a counter-clockwise DNA has the opposite sign to the corresponding clockwise DNA. But there are few theoretical studies of why these structures affect the sign of the CD spectra. In this year, we studied the CD spectrum of deoxyguansine (dG), which is one of the component molecules of DNA. The main absorption peaks were composed of π-π^* excitations but n-π^* excitations were also important for the CD spectra. The CD spectra drastically changed by the variation of the angle between deoxyribose and guanine of the nucleic acid base. Our results showed that dG would have anti-conformation in solution because the theoretical CD spectrum by the SAC-CI method agreed with the experimental spectrum if the anti-conformation was assumed in the theoretical calculation. The theoretical CD spectrum of the syn-conformation was the shape opposite to that of anti-conformation as shown in Fig. 2.

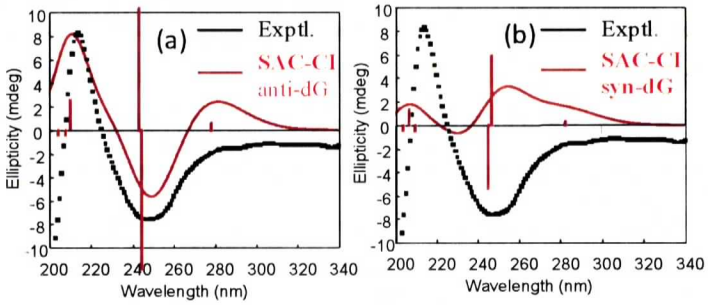

Fig. 2. Experimental (black) CD spectrum of dG, and SAC-CI (red) CD spectra of (a) anti-dG and (b) syn-dG

3. Quantum chemistry of giant molecular systems

Giant SAC/SAC-CI method that is a theory for giant molecular systems is applicable to molecular crystals. The present version of the program has rooms for improvement in its efficiency and applicability. The improvement of program is implemented by using an efficient algorithm for treating various molecules with much larger dimension.

Mechanism for a photo-induced phase transition — TTF (Tetrathiafulvalene)–CA (p-Chloranil) is a famous system in a photo-induced phase transition (PIPT). The PIPT is phenomena that the properties of the crystal drastically change by the phase transition caused by the electron transfer induced by a few photons. Their mechanisms and dynamics are interesting as a domino-toppling mechanism. Fig. 3 shows that the excitation energies and oscillator strengths of $(TTF\text{-}TCNE)_{10}$, which is a model of TTF-CA, calculated with the Giant SAC/SAC-CI method. Only the totally symmetric

excited states with the electronic structure extending over the whole crystal had a strong intensity. The whole $(TTF\text{-}TCNE)_{10}$ is going to move to r1<r2 structure in Ex1 state and to r1>r2 structure in Ex2 state. Our results suggested the possibility of concerted mechanism in PIPT rather than the previously proposed domino-toppling mechanism.

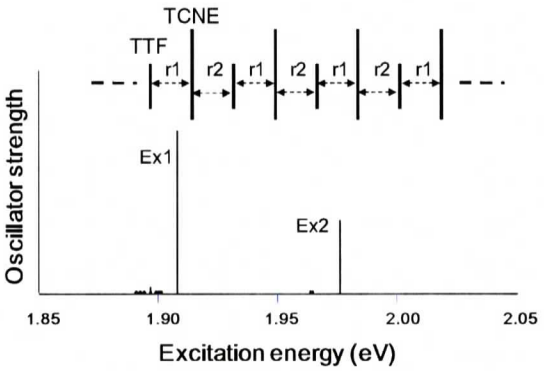

Fig. 3. The excited states of $(TTF\text{-}TCNE)_{10}$.

(Hada Group)

Magnetic Circular Dichroism and Homochirality in Bio-molecules — Magnetic circular dichroism (MCD), which is observed as circular dichroism in the presence of magnetic fields, is important as a method to analyze molecular magnetic properties especially for optically inactive molecules. In Hada Group, there are following three objectives; (a) development of programs to calculate MCD based on the SAC/SAC-CI theory which provides highly accurate calculations, (b) calculations of CD/MCD spectra for various molecules including bio-molecules, and (c) verification on the origin of homochirality in biological systems. In the present year, we made the following two progresses. (1) We accomplished the implementation of the MCD code to the SAC and SAC-CI program and applied it to some typical small molecules. This MCD code will be further improved in order to apply it to calculating and analyzing MCD spectra for larger molecules in the next term. (2) We studied the dependence of the CD spectra of an amino acid, proline, on the surrounding environments. Further we are carrying out accurate calculations of various amino acids besides alanine and proline and making systematic assignments of their CD spectra, in particular, in shorter wavelength region than vacuum UV, which might be associated with the origin of homochirality.

(Ehara Group)

Photochemistry of fluorescent molecules — The photophysical properties and the excited-state dynamics of the Ir complexes which is widely utilized as the organic light-emitting diodes have been investigated. The photo-induced electron transfer mechanism of the biological chemosensor has also been clarified.

Inner-shell electronic processes — Thermal effect observed in the O1s excitation spectrum of N_2O has been elucidated by the potential energy surfaces and the electronic part of the second moment $\langle r^2 \rangle$. The structure relaxation in the inner-shell electronic processes of CH_4, N_2O and CO_2 has been analyzed and the accurate theoretical assignment has been performed for the complex vibrational structure in the absorption spectrum. The relativistic effect of the K-shell ionization of the second-row atoms were shown to be as large as 4~9 eV by applying the scalar relativistic SAC-CI method.

Accurate theoretical spectroscopy has been performed for the excitation spectra of some haloethylenes.

Photoelectron spectra of surface-molecule interacting system — The ionization spectra of the molecules adsorbed on the metal surface has been investigated. The peak shift relative to the gas phase and the new peaks appearing in the surface- molecule interacting system were interpreted by the electron transfer from surface to adsorbates.

(Hasegawa group)

Color-tuning mechanism of human visual cone pigments — Human color vision is controlled by the red, green, and blue cone pigments. Their photo-absorption wavelengths spread uniquely over the three primary colors, although these pigments include common chromophore, retinal. In this study, we clarified for the first time molecular mechanism of color tuning in the cone pigments. The protein effect represented by the electrostatic potential is primarily important for the spectral tuning among the pigments. The structural distortion of the retinal chromophore is important in the blue pigment. The result of the analysis indicates that amino acids at specific positions in the opsins regulate the color tuning (Fig. 4).

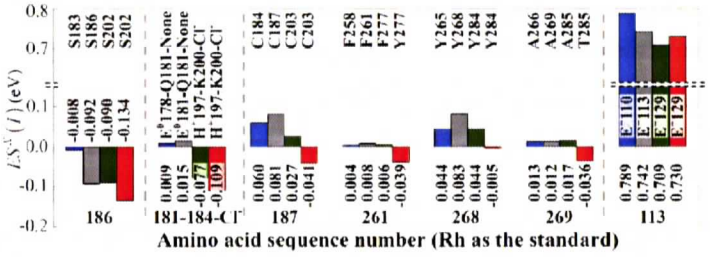

Fig. 4. Amino acid sequences important for the color tuning. The names of the residues and their ES contributions to the excitation energies in HB(blue), Rh (grey), HG (green), and HR (red). The superscripts of E and H denote the charge states of the amino acids.

§3. Formation of Research Work

Research Director or Main Research Collaborator, and Items of Research

(1) Nakatsuji group

1) Members

	Name	Affiliation	Title	Period
○	Hiroshi Nakatsuji	NPO Quantum Chemistry Research Institute	Director chairman	Oct. 2007 –
*	Ryoichi Fukuda	NPO Quantum Chemistry Research Institute	Head of division	Oct. 2007 –
*	Tomoo Miyahara	NPO Quantum Chemistry Research Institute	Head of division	Oct. 2007 –
*	Hiroyuki Nakashima	NPO Quantum Chemistry Research Institute	Head of division	Oct. 2007 –
*	Yusaku Kurokawa	Kyoto University	Graduate student	Oct. 2007 –
*	Atsushi Ishikawa	Kyoto University	Graduate student	Oct. 2007 –

	Anderson James	NPO Quantum Chemistry Research Institute	Research fellow	Jun. 2008 – Sep. 2008
	Bande Annika	NPO Quantum Chemistry Research Institute	Research fellow	Jul. 2008 –
*	Bubin Sergiy	NPO Quantum Chemistry Research Institute	Research fellow	Sep. 2008 –
*	Fan Tao	NPO Quantum Chemistry Research Institute	Research fellow	Nov. 2008 –
	Witek Henryk	National Chiao Tung University (Taiwan)	Associate professor	Jan. 2009 – Feb. 2009
	Roberto Cammi	Dipartimento di Chimica Generale Chimica Analitica, Chimica Fisica, Universita' di Parma (Italy)	Professor	Feb. 2009 –Feb. 2009
	Debashis Mukherjee	Indian Association for the Cultivation of Science, Kolkata (India)	Professor	Mar. 2009– Mar. 2009

2) Research subjects

1. Foundation of quantum chemistry as an accurate prediction science

- Exactness of the solutions of the free ICI method
- Development of the Free ICI LSE methodology and its computational algorithm
- Application of solving the Dirac-Coulomb equation for the general molecular systems

2. SAC/SAC-CI science

- Development of the direct algorithm for SAC-CI general-R method
- Methodology of theoretical CD spectroscopy and its application for biological molecules

3. Giant molecular designs

- Improvement of the Giant SAC-CI method for molecular crystals
- Mechanism of a photo induced phase transition for TTF-TCNE system

(2) Hada group

1) Members

	Name	Affiliation	Title	Period
○	Masahiko Hada	Tokyo Metropolitan University	Professor	Oct. 2007 –
	Yasushi Honda	Tokyo Metropolitan University	Research Assistant	Oct. 2007 –
	Junji Seino	Tokyo Metropolitan University	Graduate student	Oct. 2007 –

2) Research subjects

SAC/SAC-CI science

- Development of the MCD calculation programs

- Theoretical prediction on natural and magnetic circular dichroism
- Studies on the origin of homochirality in biomolecules

(3) Ehara group

1) Members

	Name	Affiliation	Title	Period
○	Masahiro Ehara	Research Center for Computational Science, National Institutes of Natural Science	Professor	Oct. 2007 −

2) Research subjects

SAC/SAC-CI science

- Photochemistry of fluorescent molecules
- Inner-shell electronic processes
- Photoelectron spectra of surface-molecule interacting system

(4) Hasegawa group

1) Members

	Name	Affiliation	Title	Period
○	Jun-ya Hasegawa	Kyoto University	Lecturer	Oct. 2007 −

2) Research subjects

SAC/SAC-CI science

- Color-tuning mechanism of human visual cone pigments

§4. Publication of Research Results

(The publication for the research results acquired in this fiscal year from this Research Theme is to be described.)

(4−1) **Publication of Thesis (The original Work)**

① Number of Publications (X times-Domestic, XX times-International)

② Detailed Information of Thesis (Name of Author, Title of Published Thesis, Journal (Name of Journal, Volume, Issue, Year of Publication) will be described.

* Note : Only Thesis of the original Work is to be described.

Number of Publications (0 times-Domestic, 19 times-International)

[1] T. Tanaka, M. Hoshino, H. Kato, M. Ehara, N. Yamada, R. Fukuda, H. Nakatsuji, Y. Tamenori,

J.R. Harries, G. Prümper, H. Tanaka, K. Ueda, "Vibration-Induced Suppression of Valence-Rydberg Mixing in the O 1s → nsσ Rydberg Series in N2O", Phys. Rev. A. 77, 012709-1-4 (2008).

[2] M. Abe, T. Suzuki, Y. Fujii, and M. Hada, "An Ab initio study based on a finite nucleus model for isotope fractionation in the U(III)-U(IV) exchange reaction system", J. Chem. Phys. **128**, 1443091-1443096 (2008).

[3] H. Nakashima and H. Nakatsuji, "Solving the electron-nuclear Schrödinger equation of helium atom and its isoelectronic ions with the free iterative-complement-interaction method", J. Chem. Phys. **128**, 154107 (2008).

[4] H. Nakashima, Y. Hijikata, and H. Nakatsuji, "Solving the electron and electron-nuclear Schrödinger equations for the excited states of helium atom with the free iterative-complement-interaction method ", J. Chem. Phys. **128**, 154108 (2008).

[5] T. Yoshizawa and M. Hada,, "Relativistic quantum-chemical calculations of magnetizabilities of noble gas atoms using the Douglas-Kroll-Hess method", Chem. Phys. Letters, **458**, 223-226 (2008).

[6] Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, "Solving the Schrödinger equation of helium and its isoelectronic ions with the exponential integral (Ei) function in the free iterative complement interaction method", Phys. Chem. Chem. Phys. **10**, 4486 (2008).

[7] M. Ehara, H. Nakatsuji, "Geometry Relaxation after Inner-Shell Electronic Excitations and Ionizations", Coll. Czech. Chem. Commun., **73**, 771-785 (2008).

[8] K. Fujimoto, J. Hasegawa, and H. Nakatsuji, "Origin of color tuning in human red, green, and blue cone visual pigments: SAC-CI and QM/MM study", Chem. Phys. Letters, **462** (4-6), 318-320 (2008).

[9] S. Arulmozhiraja, M. Ehara, H. Nakatsuji, "Electronic Transitions in cis- and trans-Dichloroethylenes and in Tetrachloroethylene", J. Chem. Phys., **129**, 174506-1-8 (2008).

[10] H. Nakashima and H. Nakatsuji, "How accurately does the free complement wave function of a helium atom satisfy the Schrödinger equation?", Phys. Rev. Lett. **101**, 240406 (2008).

[11] T. Watanabe, M. Ehara, K. Kuramoto, H. Nakatsuji, " Possible Reaction Pathway in Methanol Oxdation on Pt and Ag Surface Starting from OH Scission: Dipped Adcluster Model Study", Surface Science, **603**, 641-646 (2009).

[12] Y. Hijikata, H. Nakashima, and H. Nakatsuji, "Solving non-Born–Oppenheimer Schrödinger equation for hydrogen molecular ion and its isotopomers using the free complement method", J. Chem. Phys. **130**, 024102 (2009).

[13] M. Ehara, K. Kuramoto, H. Nakatsuji, "Relativistic Effect in the K-shell Ionizations: SAC-CI general-R Study Based on DK2 Hamiltonian", Chem. Phys., **356**, 195-198 (2009).

[14] N. Nakatani, J. Hasegawa, and H. Nakatsuji, "Artificial Color Tuning of Firefly Luminescence:

Theoretical Mutation by Tuning Electrostatic Interactions between Protein and Luciferin", Chem. Phys. Letters, **469**, 191 (2009).

[15] Y. Honda, M. Hada, "Quantum-Chemical Calculations of Natural Circular Dichroism", Computing Letters, in press.

[16] Y. Kiyota, J. Hasegawa, K. Fujimoto, B. Swerts, and H. Nakatsuji, "A multi-core QM/MM approach for the geometry optimization of chromophore aggregate in protein", J. Comp. Chem. in press.

[17] H. Nakatsuji and H. Nakashima, "How does the Free Complement Wave Function Become Accurate and Finally Exact for Hydrogen Atom Starting from the Slater and Gaussian Initial Functions and for Helium Atom on the Cusp Conditions?", Int. J. Quantum Chem. in press.

[18] M. Ehara, H. Nakatsuji, Theoretical Spectroscopy of Inner-shell Electronic Processes and Photochemistry of Fluorecent Molecules, Progress in Theoretical Chemistry and Physics dedicated to the proceedings of the 13th International Workshop on Quantum Systems in Chemistry and Physics (QSCP-XIII), in press. (23 pages) (2009).

[19] H. Nakatsuji and H. Nakashima, "Free Complement Method for Solving the Schrödinger Equation: How Accurately Can We Solve the Schrödinger Equation", The proceedings of the 13th International Workshop "Quantum Systems in Chemistry and Physics" (QSCP-XIII) in the Springer book series Progress in Theoretical Chemistry and Physics, in press.

(4－2) **Patent Application**

All the patents for the results under CREST irrespective of the applicants (Research Institutes, JST or other organizations) will be described.

① Cumulative Number

1) Patent Applications in the fiscal year 2007 (Domestic- 0 Cases, Oversea- 0 Cases)

2) Cumulative number of Patent Applications for the research period of CREST
(Domestic- 0 Cases, Oversea- 0 Cases)

3) Details for this fiscal year

a) Domestic Application (0 cases)

b) Oversea Application (0 Cases)