

**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 2006**

**Research Area :**

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

**Research Theme**

**Simulation and Dynamics of Nano- and Bio-Molecular Systems**

**Name of Research Director, Belonging and Title:**

**Kimihiko Hirao, Univ. of Tokyo, Professor**

## §1. Outline of Research Work

The primary target of the present project is to develop “The Next Generation Molecular Theory”, which provides an unambiguous way to carry out the simulations and dynamics for Nano-Scientific and Bio-molecular (Nano-Bio) systems by extending the capability of *UTChem* program package to a system with hundreds or thousands of atom. The project involves a build-up of a novel molecular theory, efficient algorithm, and software developments, which realizes the first-principle computation for Nano-Bio systems. The conventional techniques in theoretical chemistry and computational science will be incorporated to make possible the applications to Nano-Bio systems. The fundamental questions are how the complexity of the functional groups is related to its manifestation, and what are the principle and the idea in a molecular level that governs the chemical selectivity. The answer to these fundamental questions is the key ingredient to consider in the next stage to control and manifest the functionality of such systems. It is especially important that the mechanism in large systems, in contrast to moderate size of molecules, can not be interpreted in a conventional way in terms of the elementary reaction processes which comprises the reactant/product molecular structures and the reaction path connecting them; but its understanding requires dynamical averages of the relevant quantities over the equilibrium ensemble. In this study, we aim to establish the general theory and methodology to simulate the dynamical processes of large scale systems. Bio-molecules are novel nano-scale machines. The mechanism of such nano-machines is of primary interest in this study, which leads us to the design of materials with new functionality in the next stage.

The specific topics involve:

- A. *Ab initio* electronic structure theory for large systems with several hundreds to one thousand of atoms in kcal/mol accuracy.
- B. Density functional theory for large systems with ten thousands of atoms in a semi-quantative accuracy
- C. Large-scale dynamical simulations based on quantum chemistry calculations
- D. Development of *UTChem* program package for Nano-Bio systems
- E. Applications to Nano-Bio systems to understand, control, and design their functionality

In the last year, we have developed new methods for large scale systems; namely, (A), (B). In the current phase, we have made further enhancement in (A) and (B), and developed a new method for carrying out dynamics calculations, i.e., (C).

## §2. Content of Research Work

### 1. New methodologies for *ab initio* electronic structure calculations and the applications:

#### The Gaussian and finite-element Coulomb method for the fast evaluation of Coulomb integrals

We have developed a new linear scaling method for the fast evaluation of Coulomb integrals with Gaussian basis functions called the Gaussian and finite-element Coulomb (GFC) method. In this method, the Coulomb potential is expanded in a basis of mixed Gaussian and finite-element auxiliary functions that express the core and smooth Coulomb potentials, respectively. Coulomb integrals can be evaluated by three-center one-electron overlap integrals among two Gaussian basis functions and one mixed auxiliary function. Thus the computational cost and scaling for large molecules are drastically reduced. Several applications to molecular systems show that the GFC method is more efficient than the analytical integration approach that requires four-center two-electron repulsion integrals. The GFC method realizes a near linear scaling for both one-dimensional alanine *a*-helix chains and three-dimensional diamond pieces.

### 2. New Density Functional method for Large-scale Systems

#### A dual-level approach to density functional theory

We have developed an efficient approximate scheme for density-functional theory (DFT) calculations, which eliminates the time-consuming self-consistent-field (SCF) procedure using a dual-level DFT approach. In this approach, dual levels of basis sets and exchange-correlation functionals are adopted. The dual-level DFT approach is based on the idea that the total electron density in the ground state can be represented in terms of the density evaluated using the low-quality basis set and the low-cost exchange-correlation functional. Since the SCF procedure is avoided in the total energy evaluation, the dual-level DFT approach drastically reduces the computational cost. The applications of several dual-level DFT calculations to molecular systems show that our approach is more efficient than the self-consistent DFT approach with a moderate accuracy.

#### An efficient scheme of time-dependent density functional theory

We have developed a state-specific scheme for time-dependent density functional theory (SS-TDDFT) based on the Davidson algorithm. SSTDDFT is a method devised for speeding up TDDFT calculations by screening transitions that contribute to a specific excitation. By applying this method to calculations of the low-lying excitation energies of test molecules ( $\text{N}_2$ , CO,  $\text{H}_2\text{CO}$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_6\text{H}_6$ ), water clusters and polyenes, we found that SS-TDDFT accurately reproduced the excitation energies of standard TDDFT while drastically reducing the rank of the TDDFT response

matrix without loss of accuracy. We have thus formulated TDDFT that works more efficiently and economically for memory storage.

We have further developed an analytical excitation energy gradient of long-range corrected time-dependent density functional theory (LC-TDDFT). This LC-TDDFT gradient was first examined by calculating the excited state geometries and adiabatic excitation energies of small typical molecules and a small protonated Schiff base. As a result, we found that long-range interactions play a significant role even in valence excited states of small systems. This analytical LC-TDDFT gradient was also applied to the investigations of small twisted intramolecular charge transfer (TICT) systems. By comparing with calculated ab initio multireference perturbation theory and experimental results, we found that LC-TDDFT gave much more accurate absorption and fluorescence energies of these systems than those of conventional TDDFTs using pure and hybrid functionals. For optimized excited state geometries, LC-TDDFT provided fairly different twisting and wagging angles of these small TICT systems in comparison with conventional TDDFT results.

### **3. Development of novel dynamical simulation method**

We have derived coupled equations of motion of cumulants that consist of a symmetric-ordered product of the position and momentum fluctuation operators in one dimension. The key point is the utilization of a position shift operator acting on a potential operator, where the expectation value of the shift operator is evaluated using the cumulant expansion technique. In particular, the equations of motion of the second-order cumulant and the expectation values of the position and momentum operators are given. The resultant equations are expressed by those variables and a quantal potential that consists of an exponential function of the differential operators and the original potential. This procedure enables us to perform quantal (semiclassical) dynamics in one dimension. In contrast to a second-order quantized Hamilton dynamics by Prezhdo and Pereverzev which conserves the total energy only with an odd-order Taylor expansion of the potential [J. Chem. Phys. **116**, 4450 (2002); **117**, 2995 (2002)], the present quantal cumulant dynamics method exactly conserves the energy, even if a second-order approximation of the cumulants is adopted, because the present scheme does not truncate the given potential. The authors propose three schemes, (i) a truncation, (ii) a summation of derivatives, and (iii) a convolution method, for evaluating the quantal potentials for several types of potentials. The numerical results show that although the truncation method preserves the energy to some degree, the trajectory obtained gradually deviates from that of the summation scheme after 2000 steps. The phase space structure obtained by the truncation scheme is also different from that of the summation scheme in a strongly anharmonic region.

### §3. Formation of Research Work

#### (1) Univ. of Tokyo Group

##### ① Research Collaborator

	Name	Affiliation	Occupation	Participation
○	Kimihiko Hirao	Univ. of Tokyo	Professor	2005.10~
	Takahito Nakajima	Univ. of Tokyo	Associate Prof.	2005.10~
	Takao Tsuneda	Univ. of Tokyo	Associate Prof.	2005.10~
	Yasuteru Shigeta	Tsukuba Univ.	Lecturer	2005.10~
	Kiyoshi Yagi	Univ. of Tokyo	Assistant Prof.	2005.10~
*	Maho Nakata	Univ. of Tokyo	Research Fellow	2006.4~
*	G. Gopakumar	Univ. of Tokyo	Research Fellow	2006.4~
*	Mark Watson	Univ. of Tokyo	Research Fellow	2006.4~
	Minori Abe	Univ. of Tokyo	Ph.D course student	2005.10~
	Mahito Chiba	Univ. of Tokyo	Ph.D course student	2005.10~
	Seiken Tokura	Univ. of Tokyo	Ph.D course student	2005.10~
	Takeshi Sato	Univ. of Tokyo	Ph.D course student	2005.10~
	Yuki Kurashige	Univ. of Tokyo	Ph.D course student	2005.10~
	Toru Matsui	Univ. of Tokyo	Ph.D course student	2006.4~
	Jong-Won Song	Univ. of Tokyo	Ph.D course student	2006.4~

##### ② Items of Research

Kimihiko Hirao	Electronic Structure Theory based on Multireference Perturbation Theory
Takahito Nakajima	Relativistic Molecular Theory for Applications to Large-scale Systems
Takao Tsuneda	Density Functional Theory for Large-scale Systems
Yasuteru Shigeta	Molecular Theory for Large-scale systems and Molecular Dynamics on the Electronic Ground/Excited States
Kiyoshi Yagi	Vibrational Dynamics for Large Molecular Systems
Maho Nakata	Development of Density Functional Theory
G. Gopakumar	Large-scale Molecular Electronic Structure Theory
Mark Watson	Large-scale Molecular Electronic Structure Theory
Minori Abe	Large-scale Molecular Electronic Structure Theory
Mahito Chiba	Development of Large-scale Simulation methods
Seiken Tokura	Development of Density Functional Theory
Takeshi Sato	Development of Density Functional Theory
Yuki Kurashige	Large-scale Molecular Electronic Structure Theory
Toru Matsui	Development of Large-scale Simulation methods
Jong-Won Song	Development of Density Functional Theory

## §4. Publication of Research Results

### (4-1) Publication of Thesis (The original Work)

Number of Publications ( 0 times-Domestic, 16 times-International)

Detailed Information of Thesis

1. Improvement in the reaction barrier calculations of long-range-corrected density functional theory with a newly determined my parameter  
J.-W Song, T. Hirose, T. Tsuneda, and K. Hirao, *J. Chem. Phys.*, in press.
2. The Gaussian and finite-element Coulomb method for the fast evaluation of Coulomb integrals,  
Y. Kurashige, T. Nakajima, and K. Hirao, *J. Chem. Phys.*, in press.
3. Anharmonic vibrational state calculations in the electronic excited states studied by time-dependent density functional theory,  
S. Tokura, K. Yagi, T. Tsuneda, and K. Hirao, *Chem. Phys. Lett.* **436**, 30-35 (2007).
4. New implementation of molecular double point group symmetry in four-component relativistic Gaussian-type spinors,  
T. Yanai, R. Harrison, T. Nakajima, Y. Ishikawa and K. Hirao, *Int. J. Quant. Chem.*, in press.
5. Fermi resonance in CO<sub>2</sub>: an accurate prediction by electronic coupled-cluster and vibrational configuration-interaction methods,  
V. Rodriguez-Garcia, S. Hirata, K. Yagi, K. Hirao, T. Taketsugu, I. Schweigert, and M. Tasumi, *J. Chem. Phys.* **126**, 124303 (2007).
6. A theoretical study of the energetics of the reaction of triplet dioxygen with hydroquinone, semiquinone, and their protonated forms; relation to the mechanisms of superoxide generation in the respiratory chain,  
M. Bobrowski, A. Liwo, and K. Hirao, *J. Phys. Chem. B* **111**, 3543 (2007).
7. Multiple proton-transfer reactions in DNA base pairs by coordination of Pt complex,  
T. Matsui, Y. Shigeta and K. Hirao, *J. Phys. Chem. B* **111**, 1176 (2007).
8. Long-range-corrected time-dependent density functional study on fluorescence of of 4,4'-dimethyl-Aminobenzonitrile,  
M. Chiba, T. Tsuneda, and K. Hirao, *J. Chem. Phys.* **126**, 034504 (2007).
9. Relativistic coupled-cluster calculation of parity non-conservation (PNC) in Ba<sup>+</sup>,  
G. Gopakumar, B. P. Das, R. K. Chaudhuri, D. Mukherjee, and K. Hirao, *J. Chem. Phys.* **126**, 014301 (2007).
10. Quantal cumulant dynamics,  
Y. Shigeta, H. Miyachi, and K. Hirao, *J. Chem. Phys.* **125**, 244102 (2006).
11. Real time mixed quantum-classical dynamics with ab initio quartic force field: Application to molecular vibrational frequency analysis,

- H. Miyachi, Y. Shigeta, and K. Hirao, Chem. Phys. Lett **432**, 585 (2006).
12. The relativistic complete active space second order perturbation theory (CASPT2) with the four-component Dirac Hamiltonian,  
M. Abe, T. Nakajima, and K. Hirao, J. Chem. Phys. **125** 234110 (2006).
  13. Influence of Pt complex binding on the guanine cytosine pair: A theoretical study,  
T. Matsui, Y. Shigeta and K. Hirao, Chem. Phys. Lett. **423**, 331 (2006).
  14. Franck-Condon factors based on anharmonic vibrational wave functions of polyatomic molecules,  
V. Rodriguez-Garcia, K. Yagi, K. Hirao, S. Iwata, and S. Hirata, J. Chem. Phys. **125**, 014109 (2006).
  15. Theoretical Study of Valence Photoelectron Spectra of  $\text{Re}(\text{CO})_5\text{X}$  (X = Cl, Br, and I):  
A Spin-Orbit DK3-SAC/SAC-CI Study,  
T. Nakajima, S. Hane, and K. Hirao, J. Chem. Phys. **124**, 224307 (2006).
  16. Exact-exchange time-dependent density-functional theory with the frequency-dependent kernel,  
Y. Shigeta, K. Hirao, S. Hirata, Phys. Rev. A **73**, 010502 (2006).

#### (4-2) Patent Application

##### ① Cumulative Number

- 1) Patent Applications in the fiscal year 2006 (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)