JST Basic Research Programs
CREST
(Core Research for Evolutional Science and Technology)

Annual Report for Research Work in the fiscal year 2005

Research Area :
High Performance Computing for Multi-scale and Multi-physics Phenomena
Research Theme
Simulations and Dynamics for Nanoscale and Biological 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 algorism, 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-quantitative accuracy
C. Large-scale dynamical simulations based on quantum chemistry calculations
D. Relativistic molecular theory for large scale molecular systems
E. Development of *UTChem* program package for Nano-Bio systems
F. Applications to Nano-Bio systems to understand, control, and design their functionality

In the first phase of the present project, we focused on developing new methodolgies for large scale systems; namely, (A), (B) and (D).

§2. Content of Research Work

1. New methodologies for *ab initio* electronic structure calculations and the applications: Development of fast two-electron integrals

We have developed the adaptive density partitioning technique (ADPT) method for the efficient evaluation of the Coulomb matrix elements. While we use the extant technique that is based on the density fitting using an auxiliary plane wave basis set, our independent improvement appears in the way of density partitioning that strongly affects the efficiency of the auxiliary plane wave method. We have tried to describe as many Gaussian pairs, which are components of the density, as possible by auxiliary plane waves by using the new criteria that is based on the error estimation and able to control the accuracy and efficiency. We are able to drastically reduce the number of core Gaussian products, which cannot be readily described by plane wave basis sets and are left in the Gaussian representation, compared with the exponent partitioning methods. In the taxol molecule with the 6-31G** basis, the necessary two electron integrals are reduced to 11%. Our adaptive partitioning is applicable to the other type of auxiliary basis sets that are not adequate for the core electrons; the ADPT is not only for plane waves. With the ADPT, we can reduce the core Gaussian products and its analytical integrals by using the accurate grid, but the plane waves are not suitable for this purpose because the number of uniform grids increases rapidly for the refinement. In contrast, finite element can be efficiently refined with a minimum of increase in number. The ADPT with the auxiliary finite-element is now in progress.

2. New Density Functional method for Large-scale Systems

The long-range correction (LC) scheme of density functional theory (DFT) was applied to the calculation of the π-aromatic interaction of benzene dimer. In previous calculations, it was confirmed that the LC scheme [Iikura et al., J. Chem. Phys., 115, 3540, 2001] gives very accurate potential energy surfaces (PES) of small vdW complexes by combining with a vdW correlation functional (LC-DFT+ALL). In this study, LC-DFT+ALL method was examined by calculating a wide range of PES of the benzene dimer including parallel, T-shaped, and parallel-displaced configurations. As a result, we succeeded in reproducing very accurate PES within the energy deviance of less than 1 kcal/mol in comparison with the results of high-level ab initio molecular orbital methods at all reference points on the PES. It was also found that LC-DFT+ALL gave accurate results independent of exchange-correlation functional used, in contrast to the strong functional dependencies of conventional pure functionals. This indicates that both exchange repulsion and van der Waals attractive interactions should be correctly incorporated in conventional pure functionals in order to calculate accurate π-aromatic interactions. We also found that

LC-DFT+ALL method has a low basis-set dependency in the calculations of π-aromatic interactions. This may suggest that LC-DFT+ALL method would be a powerful tool in calculations of large molecules such as biomolecules.

To theoretically investigate photoreactions of large-scale molecules, we require a excited-state theory that reproduces accurate charge transfer excitations in a short time. Time-dependent DFT (TDDFT) is one of high-speed excited-state calculation theories. However, it has been recently suggested that TDDDFT gives poor charge transfer energies. We recently applied the LC scheme to TDDFT and succeeded to solve this problem. In this study, we derived the analytical gradient form of LC-TDDFT and implemented it on a calculation program. By calculating various excited-state structures and excitation energies, we confirmed that LC-TDDFT obviously gave very accurate results especially for charge transfer systems. We also applied LC-TDDFT to investigations of the dual fluorescence mechanism of 4-(N,N-dimethylamino)benzonitrile (DMABN) molecule. It is known that DMABN emits red-shifted dual fluorescence in polar solvent, although it emits single fluorescence in gas phase and in nonpolar solvent. As a result, we found that LC-TDDFT revealed the whole mechanism of the dual fluorescence. The present calculations showed that the main peak in the dual fluorescence clearly comes from the twisted intramolecular CT state, and remarkably, the secondary peak may be also emitted from the CT state in the middle way of the twisting.

3. Development of relativistic electronic structure theory and its application

The relativistic effects in quantum systems are theoretically taken into account by solving the Dirac equation, instead of the non-relativistic Schrödinger equation. In the Dirac equation, the wave function has four components which considerably increases the computational cost, and its application has been limited to small molecular systems. In order to break through this limitation, we have been developing the molecular theory based on the relativistic four-component Hamiltonian, and on the approximate relativistic Hamiltonian.

In the non-relativistic calculations, there have been proposed several effective schemes to carry out MP2 calculations. In this work, we have developed a new type of MP2 method which incorporates Resolution of Identity Local Laplace-transformation, denoted as RILL-MP2. Test applications have shown that the present method can reproduce the conventional MP2 energy and properties with much greater efficiency, indicating the capability for larger molecular systems. Furthermore, it has been shown that the accuracy is maintained in a certain level irrespective to the size of the system. The extension of the present scheme to the relativistic regime is now in progress.

§3. Formation of Research Work

（1）Univ. of Tokyo Group

①Research Collaborator

	Name	Affliction	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	Univ. of Tokyo	Assistant Prof.	2005.10～
	Kiyoshi Yagi	Univ. of Tokyo	Assistant Prof.	2005.10～
	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～

②Items 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
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

§4. Publication of Research Results

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

① Number of Publications (0 times-Domestic, 3 times-International)

② Detailed Information of Thesis

1) Excited state geometry optimizations by analytical energy gradient of long-range corrected time-dependent density functional theory,
   M. Chiba, T. Tsuneda; and K. Hirao, J. Chem. Phys. **124**, 144106 (2006).
2) An approximate second order Moeller-Plesset perturbation approach for large molecular calculations,
   T. Nakajima and K. Hirao, Chem.Phys. Lett., in press.
3) A dual-level approach to density functional theory,
   T. Nakajima and K. Hirao, J. Chem.Phys., in press.

（4－2） Patent Application

① Cumulative Number

1) Patent Applications in the fiscal year 2005 (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)