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 2005

Research Area :

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

Research Theme

Theoretical Studies of the Charge Transfer Mechanisms in Biological Systems with QM (MRSCI+DFT)/MM methods

Name of Research Director, Belonging and Title:

Toshikazu TAKADA, Fundamental and Environmental Research Laboratories, NEC Corporation, Research Fellow

§1. Outline of Research Work

Learning effective metabolic mechanisms of biological systems is considered to be useful to produce industrial materials in safe manners with high energy efficiency, and consequently to construct sustainable societies adjusted to the future environment. Recent experimental technologies as seen in X-ray and electron beam structure analyses have been revealing the nature of biological systems at molecular levels, which is surprisingly sophisticated and well organized. One of such chemical phenomena is charge separation occurring between molecules which are parts of the biological systems.

The objectives of this project are:

1. To develop a computer program for bio-molecular simulations specially aimed at investigations of mechanisms of electron transfer in the biological systems
2. To study the charge separation mechanism occurring in the photosynthetic reaction center by using the program.

QM/MM (Quantum Mechanics/Molecular Mechanics) is realized to be an effective scheme to carry out molecular orbital calculations on large molecules such as proteins. That is, the computer time will be drastically reduced by applying the quantum mechanical methods only to the restricted molecular region in which an interested chemical reaction occurs, and the molecular mechanics to the rest of the molecular system, which is much larger than the QM space. Therefore, in this project, MRSCI (Multi Reference Single Electron Excited Configuration Interaction) hybridized with DFT is taken as a QM theory which is an appropriate scheme to handle excited states which are essential in the electron transfers.

§2. Content of Research Work

To achieve QM/MM calculations on electron transfers in the biological systems, the following functionalities are needed:

1. Correct description of the QM space by MRSCI scheme
2. Hybridization with DFT to take account of dynamic electron correlations
3. Evaluation of interactions with atoms and molecules in the MM region by empirical potentials

These are developed respectively, by NEC Fundamental and Environmental Research Laboratories, Graduate School of Science of Osaka University and Institute for Protein Research of Osaka University.

Here, an MRSCI package should have a capability to handle more than 6 thousand basis functions with the dimension of nearly 100 millions as the size of CSF's, since 6 pigments such as chlorophyll in the reaction center are involved in the charge separation. The diagonalization code was developed this year, following Davidson's algorithm. From the benchmarks, it was found that Davidson's method was quite efficient for the MRSCI calculations.

The memory size was checked up to 30 million dimension due to the memory limitation of PC cluster. For the 30 million, the memory of 240 MB is used to obtain one eigen value. Since this is proportional to the dimension of CI, roughly 800 MB is requested for the calculation of the reaction center, which is feasible. The computing time for that case is less than 10 seconds even on one processor. Therefore, this diagonalization package is understood to be adequate for MRSCI calculations.

To see a rough image of the excited sates of chlorophyll dimmer, CAS-CI was carried out, It was found that the electronic structures of the excites states are quite complicated, resulting the MRSCI approach will be useful to understand the electron transfer mechanism.

Next, the hybridization with DFT is described. The major issue to hybridize MRSCI with DFT is how to overcome so called double count problem, that is, how to eliminate dynamic electron correlations from DFT formulation, which are automatically taken in the wave function expansion of MRSCI. This year, the equation for it was formulated, in which the correlations are divided to two terms, i.e., one expressed by the wave function expansion and the other describe by DFT called "residual correlation". Following this formulation, the computer code will be developed next year

To establish the QM/MM simulations on bio-related compounds, the effects from surrounding proteins, solvents and other materials are to be taken into account. Usually, the periodic boundary condition method is used for it. Here, Nakamura, one of the collaborators, invented a method to reproduce such effects of those materials to the atoms and molecules in the QM space by using point charges and point dipoles on the closed surface covering the region. This approach is expected to reduce the computer time in order to take the effects into account.

Next year, those three different methods are hybridized into one simulation system and tests on small molecular systems are carried out to see how appropriate this is to study the electron transfer in the biological systems.

§3. Formation of Research Work

Name: Toshikazu Takada
Title: Research Fellow
Affiliation: Fundamental and Environmental Research Laboratories, NEC Corporation
Research Subject: Development of MRSCI Code and Application to Photosynthetic Reaction Center to Study the Charge Separation Mechanism

Name: Kizashi Yamaguchi
Title: Professor
Affiliation: Graduate School of Science, Osaka University

Research Subject: Developments of MR-DFT and MRSCI Theories and Their Computer Programs

Name: Haruki Nakamura

Title: Professor

Affiliation: Institute for Protein Research, Osaka University

Research Subject: Development of Computer Programs based on Molecular Mechanics to Take Account of Surrounding Proteins and etc to QM Region

§4. Publication of Research Results

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

① Number of Publications (0 papers in Domestic journals, 0 papers in International journals)

（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)