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

Construction of Nano-Architecture Based on Computational Quantum Theoretical Sciences

Name of Research Director, Title and Affiliation:

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Professor

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§1. Outline of Research Work

Quantum effects are important in phenomena in nano-meter scale structures. The aim of the present research project is to improve current methodology in quantum simulations dramatically, to establish new methodology for nano- and bio-materials consisting of a large number of atoms, and then to construct nano-architecture in materials based on obtained scientific knowledge. In 2006 fiscal year, we have tuned our code based on the real-space density functional theory, which was developed in 2005 fiscal year as a major tool to overcome a multi-scale problem in space, and achieved the high performance on parallel computers. As for a multi-scale problem in time, we have combined the Car-Parrinello Molecular Dynamics method with Meta-dynamics, and performed quantum dynamical simulations for biochemical reactions in proteins. Further we have simulated dynamics of excited carriers in carbon nanotubes using our FPSEID code based on the time dependent density functional theory. We have also studied relation among atomic structures, nano-scale shapes, electronic properties and functions in variety of materials including defects and interfaces of semiconductors, carbon nanotubes and related materials, on the basis of the density functional theory. In 2007 fiscal year, we plan to further improve the methodology in a sophisticated manner and perform quantum simulations for a variety of materials.

§2. Content of Research Work

In this research project, there are two aspects which should be considered simultaneously: One is development and sophistication of methodology and the other is clarification and prediction of phenomena in nano- and bio-materials. In the former aspect, we have worked on improvement and sophistication of the Real-Space Density-Functional Theory (RSDFT) code and the Car-Parrinello Molecular Dynamics (CPMD) plus the Meta-Dynamics code (CPMD-MeD) in 2006 fiscal year. The collaboration between physical science and computer science in our group has assisted in the good progress. In the latter aspect, based on several schemes including the above within the frame work of the density functional theory (DFT), we have performed clarification and prediction of phenomena in semiconductors, carbon nano-materials and proteins.

A new scheme that describes van der Waals interaction within the DFT, which is important in biomaterials, is on the way to the goal, however, and require more efforts in coming years.

The followings are excerpts of our achievements in 2006 fiscal year.

1. Tuning of RSDFT and its Application on the Parallel Computer PACS-CS

   RSDFT in which all the quantities are computed on lattice points in real space is free from communication burdens such as FFT and is also capable of treating any boundary conditions like periodic or non-periodic on computation cells. This makes RSDFT a candidate for a major simulation tool in next-generation supercomputers. In 2006 fiscal year, we have tuned our RSDFT code, which was developed in 2005 fiscal year, on the parallel computer PACS-CS (Center for

Computational Sciences, University of Tsukuba: 1 node = 5.6 GFLOPS, 2560 nodes). The important progress includes:

(i) We have changed an algorithm to perform Gram-Schmidt orthogonalization, thus reduced it to a form of matrix-times-matrix operations, and hereby accelerated this order-N**3 part tremendously. The resulting performance using 256 nodes is 64 % of the theoretical peak performance of the nodes.

(ii) We have adopted the divide-and-conquer algorithm to treat partial diagonalization and achieved the net performance of 71 %.

We now apply this RSDFT to issues of atomic structures of defects in Si and formation of 90-degree dislocations in stressed Ge films, which are both important in semiconductor technology.

2. Mechanisms of Bio-Chemical Reactions in Proteins by CPMD-MeD

1) Proton transfer in cytochrome c oxidase

The protein named cytochrome *c* oxidase exists in membrane of mitochondria and, at the final stage of respiration activity, is responsible for proton transfer by which energy for subsequent ATP synthesis is provided. We proposed a mechanism of proton transfer through peptide bonds in 2005 fiscal year. In 2006, we have performed detailed CPMD-MeD simulations for possible atomic reactions involved in the proton transfer and found that the transfer takes place in a concerted manner participated by adjacent peptide bonds. The calculated free-energy barrier agrees with the experiment (Fig. 1).

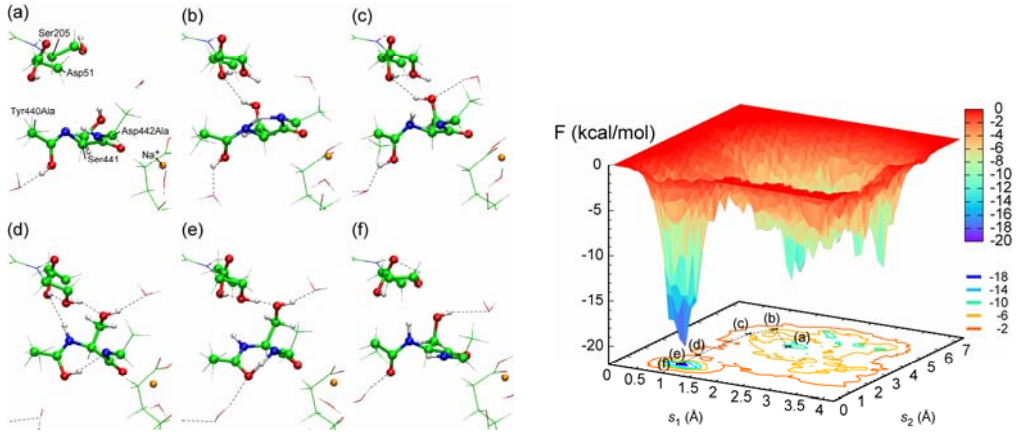

Fig.1: Proton transfer through peptide bonds in cytochrome c oxidase. The reaction process in the left figure. The lower proton (white ball) between Tyr440 and Ser441 moves to the upper region through (a) to (f), interacting with oxygen (red), carbon(green) and nitrogen (blue) atoms. In the right figure, calculated free-energy landscape is shown.

2) Decomposition of ATP in HSC (Heat Shock Cognate) 70 protein

HSC70 is a one of proteins which protect cells from various stresses. Stress induces decomposition of ATP in the protein and thereby the protein changes its shape to protect stressed cells. Yet the mechanism for the protein decomposition has been unknown. In this year, we have clarified that the decomposition is a concerted hydrolysis reaction in which surrounding water molecules and mono- and di-valent metallic ions participate. The calculated free-energy barrier fairly agrees with the experiment. In this calculation, a QM/MM hybrid technique as well as CPMD-Med has been used to simulate 50730 atoms.

3. Relaxation of Excited Carriers in Carbon Nanotubes by FPSEID

Carrier relaxation and ion dynamics upon electron excitation are fundamental issues in materials science. We have performed such simulations for carbon nanotubes in this year using FPSEID (First-Principle Simulation tool for Electron-Ion Dynamics). We have clarified that excited carriers (electrons and holes) releases their energies by surfing various adiabatic surfaces and radial breathing modes of ions are excited during the carrier relaxation.

4. Calculation of Materials using DFT

1) Role of selective hybridization at interfaces in Schottky barriers

It has been recognized that Schottky barriers at metal/semiconductor or metal/insulator interfaces are primarily determined by the workfunction of the metal and the electron affinity of the semiconductor (insulator), and they are modified by electric double layer generated at the interfaces. In recent experiments for metal/high-k insulator/semiconductor MOS structures, however, observed Schottky barriers are unable to be explained by the conventional concept above. We have shown that the observed barriers are beautifully explained by a new idea that electron states of the metal are hybridized selectively with particular atomic orbitals in the insulator.

2) Electronic structure theory for reactions near nano-scale interfaces

We have found that two interfaces in MOS structures, i.e., metal/oxide and oxide/semi-conductor interfaces, are correlated when oxide films become as thin as nanometers. Suppose some reaction at the oxide/semiconductor takes place and generate a vacancy. When an electronic level induced by the vacancy is located at higher position, then the electron is transferred to the Fermi level in the metal and hereby modifies the Schottky barrier at the metal/oxide interface. We have indeed shown that this is the case for metal/HfO_2/Si structures. Photoemission experiments performed for TiN/HfO_2/Si have confirmed this theoretical prediction.

3) Magnetism due to topological defects in carbon nanotubes

We have found that carbon nanotubes with topological line defects consisting of 5-membered and 8-membered rings exhibit ferromagnetic ordering along the line (Fig. 2). This

is due to electron accommodation in flat bands generated by a balance between wavefunctions extending along the line. In that sense this magnetism is clearly different from usual magnetism in transition metal or organic conductors.

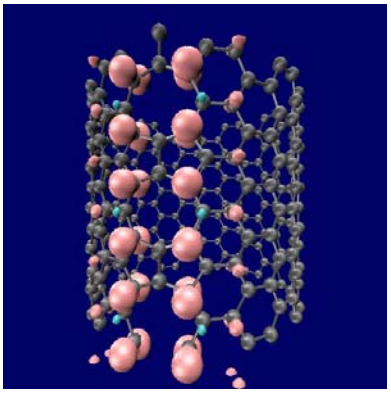

Fig.2 : Clouds of spin density in carbon naotubes which have a linear topological defect consisting of 5-membered and 8-membered carbon networks. We observe spin density along the line defect.

4) Capacitance of double-walled carbon nanotubes

It becomes important to identify physical quantities in nano-structures in future technology. Capacitance is an example. We have formulated a scheme to calculate capacitance based on DFT and applied it to a nano-capacitor composed of double-walled carbon-nanotubes. We have found two quantum effects become prominent: sensitive dependence of capacitance on bias voltage and substantial enhancement of capacitance.

§3. Formation of Research Work (organization of research group)

(1) Group at University of Tsukuba

① Members

	Name	Affiliation	Title	Period
○	Atsushi Oshiyama	University of Tsukuba	Professor	H17.10～
○	Kenji Shiraishi	University of Tsukuba	Associate Professor	H17.10～
	Mauro Boero	University of Tsukuba	Associate Professor	H17.10～
	Masaru Tateno	University of Tsukuba	Associate Professor	H17.10～
	Susumu Okada	University of Tsukuba	Associate Professor	H17.10～
	Daisuke Takahashi	University of Tsukuba	Associate Professor	H17.10～
	Savas Berber	University of Tsukuba	Research Associate	H17.10～
	Jung Mee Park	University of Tsukuba	Research Associate	H 18.4～
	Jun-ichi Iwata	University of Tsukuba	Post-doctoral fellow	H17.10～
＊	Katsumasa Kamiya	University of Tsukuba	Post-doctoral fellow	H17.10～
＊	Yoshitaka Fujimoto	University of Tsukuba	Post-doctoral fellow	H18.4～
＊	Kazuyuki Uchida	University of Tsukuba	Post-doctoral fellow	H18.4～
	Takahiro Kurita	University of Tsukuba	Graduate student	H18.4～

② Research issues

- Developments of methodology and its applications to quantum simulations for 10 -100 thousands of atoms
- Developments of HPC technique in quantum simulations for nano- and bio-materials
- Developments of a new method to describe dispersion forces in bio-materials and its

application

- Developments of methods for function-simulations in nano- and bio-materials

(2) Group at NEC Corporation

① Members

	Name	Affiliation	Title	Period
○	Yoshiyuki Miyamoto	NEC Laboratories	Principal researcher	H17.10～

② Research issues

- Developments of methodology to describe electron excitation and ion dynamics and its application

(3) Group at ETHZ

①Members

	Name	Affiliation	Title	Period
○	Michele Parrinello	ETH Zurich	Professor	H17.10～
	Alessandro Laio	ETH Zurich	Researcher	H17.10～
	Francesco L. Gervasio	ETH Zurich	Researcher	H17.10～
	Marcella Iannuzzi,	Zurich University	Researcher	H17.10～

②Research Issues

- Application of CPMD with metadynamics
- Innovation of CPMD

§4. Publication of Research Results (Publications in the Project)

（4－1） Publication of Thesis (The original Work) , i.e., Original Papers

① Number of Publications (0 in domestic journals, 14 in international journals)

② Detailed Information of original papers

1) S. Okada, K. Nakada, K. Kuwabara, K. Daigoku, and T. Kawai, ``Ferromagnetic Spin Ordering on Carbon Nanotubes with Topological Line Defects" Phys. Rev. B **74**, art. no. 121412(R) (2006).

2) S. Okada, K. Nakada, and T. Kawai, ``Orientation Dependence of Magnetic Moment of Carbon Nanotubes with Topological Line Defects" Appl. Phys. Lett. **90**, art. no. 103120 (2007).

3) S. Okada, ``Radial-Breathing Mode Frequencies for Nanotubes Encapsulating Fullerenes", Chem. Phys. Lett. **438**, 59 (2007).

4) S. Hino, M. Kato, D. Yoshimura, H. Moribe, H. Umemoto, Y. Ito, T. Sugai, H. Shinohara, M. Otani, Y. Yoshimoto and S. Okada, ``Effect of Encapsulated Atoms on the Electronic Structure of the Fullerene cage: A Case Study on $La_2@C_{78}$ and $Ti_2C_2@C_{78}$ via Ultraviolet Photoelectron Spectroscopy", Phys. Rev. B **75**, 125418 (2007) .

5) M. Oshikiri and M. Boero, ``Water Molecule Adsorption Properties on the $BiVO_4$ (100) Surface", J. Phys. Chem. B **110**, 9188 (2006).

6) F. L. Gervasio, M. Boero and M. Parrinello, ``Double Proton Coupled Charge Transfer in DNA" , Angew. Chem. Int. Ed. **45**, 5606 (2006).
7) L. M. Ramaniah and M. Boero, ``Structural, Electronic, and Optical Properties of the Diindenoperylene Molecule from First-Principles Density Functional Theory", Phys. Rev. A **74**, 042505 (2006)
8) M, Boero, T. Ikeda, E. Ito and K. Terakura, ``Hsc70 ATPase: An Insight into Water Dissociation and Joint Catalytic Role of K^+ and Mg^{2+} Metal Cations in the Hyrolysis Reaction", J. Am. Chem. Soc. **128**, 16798 (2006).
9) M. Boero, F. L. Gervasio and M. Parrinello, ``Charge Localisation and Hopping in DNA", Mol. Simul. **33**, 57 (2007).
10) T. Ikeda, M. Boero and K. Terakura, ``Hydration of Alkali Ions from First Principles Molecular Dynamics Revisited", J. Chem. Phys. **126**, 034501 (2007).
11) Y. Akasaka, G. Nakamura, K. Shiraishi, N. Umezawa, K. Yamabe, O. Ogawa, M. Lee, T. Amiaka, T. Kasuya, H. Watanabe, T. Chikyow, F. Ootsuka, Y. Nara, and K. Nakamura, "Modified Oxygen Vacancy Induced Fermi Level Pinning Model Extendable to P-Metal Pinning", Jpn. J. Appl. Phys. Part 2, **45**, L1289 (2006).
12) Uedono, T. Naito, T. Otsuka, K. Shiraishi, K. Yamabe, S. Miyazaki, H. Watanabe, N. Umezawa, T. Chikyow, Y. Akasaka, S. Kamiyama, Y. Nara, and Yamada, "Introduction of defects into HfO_2 gate dielectrics by metal-gate deposition studied using x-ray photoelectron spectroscopy and positron annihilation", J. Appl. Phys. **100**, Art. No. 064501 (2006).
13) K. Shiraishi, K. Yamada, K. Torii, Y. Akasaka, K. Nakajima, M. Konno, T. Chikyow, H. Kitajima, T. Arikado and Y. Nara, ``Oxygen-Vacancy-Induced Threshold Voltage Shifts in Hf-Related High-k Gate Stacks" Thin Solid Films, **508**, 305 (2006).
14) H. Yamaguchi, M. Tateno, and K. Yamasaki, ``Solution structure and DNA-binding mode of the matrix attachment region-binding domain of the transcription factor SATB1 that regulates the T-cell maturation" J. Biol. Chem., **281**, 5319 (2006).

(4－2) Patent Application

① Cumulative Number

1) Patent Applications in the fiscal year 2006

NONE

2) Cumulative number of Patent Applications for the research period of CREST

NONE