

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

**Construction of Nano-Architecture Based on Computational Quantum Theoretical
Science**

Name of Research Director, Belonging and Title:

**Atsushi OSHIYAMA, Graduate School of Pure and Applied Sciences /
Center for Computational Sciences, University of Tsukuba, Professor**

§1. Outline of Research Work

Quantum effects manifest themselves in phenomena in nano-meter scale structures and thus new properties and functions are expected to emerge. 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 10 – 100 thousands atoms, and then to construct nano-architecture in materials based on obtained scientific knowledge. In 2005 fiscal year, we have developed a new program code for the real-space density functional theory which is regarded as a major method to simulate large-scale systems, and then performed computations for a 4000-atom system. In order to overcome a multi-scale problem in time, we have combined a Car-Parrinello Molecular Dynamics method with Meta-dynamics, and performed quantum dynamical simulations more than picoseconds for biomaterials consisting of several hundreds of atoms. Based on the methods described above and with other methods based on the density functional theory, we have studied correlation among atomic structures, nanoshapes, electronic and physical properties and occurrence of functions in nano- and bio-materials such as high-k films, carbon nanotubes and cytochrome oxidase. In 2006 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 project, there are two research aspects which should be performed simultaneously: One is development of methodology and the other is clarification and prediction of phenomena in nano- and bio-materials. In the former aspect, we have (1) developed a Real-Space Density-Functional Theory (RSDFT) code, and (2) implemented Meta-dynamics approach in Car-Parrinello Molecular Dynamics (CPMD) method in this fiscal year. In the latter aspect, based on the density functional calculations, we have done (1) clarification of fundamental properties of HfO_2 which is the most promising high dielectric-constant material in next-generation silicon technology. (2) clarification and prediction of new properties of hybrid structures consisting of carbon nanotubes and conventional materials such as Si and metals, (3) exploration of proton pathways in cytochrome c oxidase which is responsible for energy conversion in life system. The followings are excerpts.

1. Development of the real-space density functional code and its application to defects in Si

Development of the first version of our RSDFT code has been finished. In the first version, a part of treating non-local parts of pseudo-potentials is done in real space so that $O(N^2)$ scaling is realized. Also Fourier transformation is unnecessary since Hamiltonian operation is done in real

space. In solving Kohn-Sham equation, a conjugate gradient minimization scheme and a residual minimization scheme are used to make the code faster.

Using this RSDFT code, structural determination of the di-vacancy in Si has been performed. Based on the electron-spin-resonance experiments, it is argued that 6 neighboring atoms around the di-vacancy exhibit pairing structural relaxation. Yet extremely large pairing is necessary in order to explain symmetry of experimentally observed wave-functions of deep levels. Then Saito and Oshiyama [PRL **73**, 866 (1994)] argued a new relaxation pattern called resonant bonds based on the density functional calculations. Another density functional calculations supported the large pairing relaxation, however [Ögüt and Chelikowski: PRL **83**, 3852 (1999)]. It is therefore meaningful to perform large scale calculations by RSDFT to put a light on this confusion. The present RSDFT calculations have been done systematically from 64-site to 1000-site systems. It is found that more than 512 sites around the di-vacancy are enough to get structural relaxation patterns and that the large pairing relaxation does not appear in this system.

2. Meta-dynamics approach to proteins

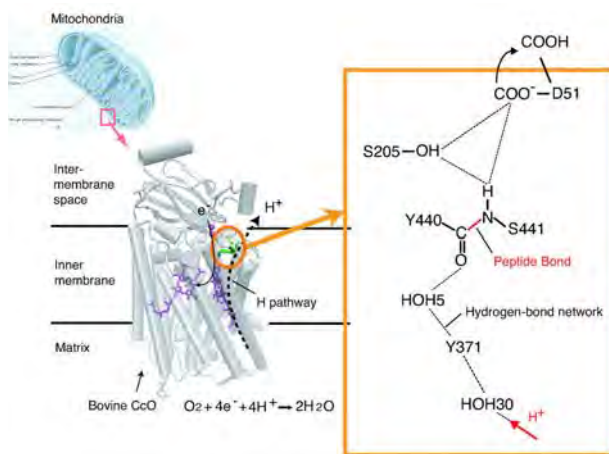


Fig 1: Schematic view of proton transfer in cytochrome *c* oxidase located in mitochondria membrane. Proton transfer takes place through peptide bonds between Y440 and S441. ATP is synthesized efficiently using chemical potential difference induced by this proton transfer.

Implementation of Meta-dynamics approach in CPMD scheme has been finished. As an application of this method, we have studied mechanisms of proton transfer in cytochrome *c* oxidase which is located in a mitochondrion membrane and is responsible for energy conversion of our life systems. Proton transfer is known to take place via hydrogen bonding in sequences of water molecules (Grotthuss mechanism). In cytochrome *c* oxidase, however, the water sequence is interrupted by peptide bonds (Fig 1). Our metadynamics-CPMD calculations has clarified that keto-enol tautomerization reactions take place around the peptide bond, hereby accomplishing cycles of proton transfer, and that a turned structure of the protein is important to reduce reaction barriers in a concerted manner.

3. Properties of next-generation insulating films HfO₂

In the miniaturization of silicon technology, one of the most urgent tasks is exploration of high-dielectric-constant (high-k) materials and clarification of their feasibility in fabrication of current technology. The most promising material at present is HfO_2 . We have done the density functional calculations for oxygen vacancies in HfO_2 . We have found that a deep level induced by the O vacancy appears at 1 – 1.6 eV below the conduction band bottom in its neutral state, whereas the level appears near the conduction band bottom in its +2 charge state.

This means that electrons injected in HfO_2 with the oxygen vacancy are trapped by the deep level induced by the O vacancy. It is actually observed that stress-induced-leakage-current increases via deep levels upon electron injection.

We have further performed the DFT calculations for interactions between the O vacancies and nitrogen atoms. It has been found that the nitrogen is selectively located near the O vacancy and hereby erases the deep levels. This corresponds to the experimentally observed decrease of leakage currents upon nitrogen doping.

From these DFT calculations, it has been proposed that the p-type Si which has been used as an electrode is unsuitable in the next generation Si technology since control of threshold voltage in MISFET becomes extremely difficult in Si/ HfO_2 junctions. A new transistor with Ta-silicide as an electrode has been developed in Selete where Professor Shiraishi in this project is also a member.

4. Structural imperfection of carbon nanotubes

A lot of research activities have been done for carbon nanotubes (CNTs) because of their fascinating physical properties and uniqueness of their nano-shapes. Yet structural imperfection of CNTs has been less studied so far. We have investigated atomic structures, electron states and spin states of mono- and di-vacancies in CNTs with diameters ranging from 4 Å to 9 Å using the density functional theory. It has been found that there are several meta-stable structures separated to each other by small energy barriers in the mono-vacancy, and that energy gain upon relaxation of surrounding atoms is substantial (5 eV for the mono-vacancy and 3 – 6 eV for the di-vacancy), thereby exhibiting a self-healing character. We have also found that spin-polarized states emerge in several atomic structures for the mono- and the di-vacancies.

We have further explored structural modification upon introduction of aggregates of vacancies. Our density-functional calculations show a surprise. In CNTs with aggregates of di-vacancies, bonds are repaired without any energy barrier. The resulting new bond network consists of carbon pentagons and octagons with all the carbon atoms three-fold coordinated. A new electron states confined in the sequence of pentagons and octagons emerges and induces a certain magnetic ordering.

5. Hybrid structures of carbon nanotubes and conventional materials

One of the applications of CNTs may exist in nano-electronics. From such viewpoints, clarification of electronic and physical properties of hybrid structures of CNTs and Metal electrodes or semiconductor substrates becomes extremely important.

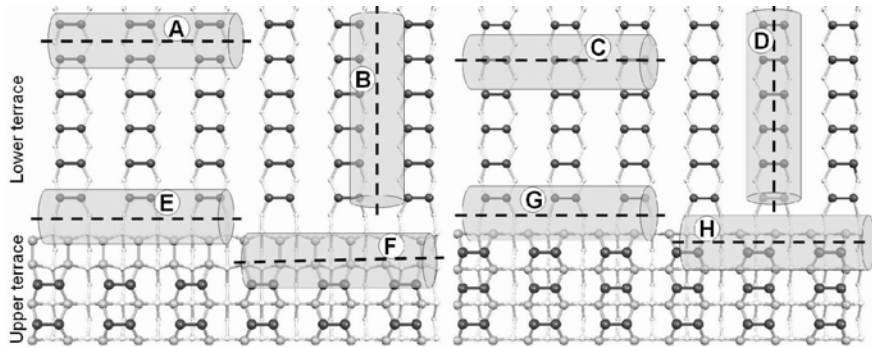


Fig 2: Various sites of CNTs adsorbed on Si(001) surface. A, B, C and D are the sites on terraces, whereas E, F, G and H are the sites near double-layer step edges (lower part of the figure is the upper terrace) .

In this fiscal year, we have explored a possibility of placing CNTs regularly on semiconductor surfaces using the density functional theory. We considered Si(001) surface. For a thin (5,5) CNT, it has been found that the site on the terrace is most stable with the binding energy being 2.77 eV and that the next most stable is the site along step edges with the binding energy being 1.88 eV. The binding energies should depend on tube radii and thicker tubes favor step edges. In the Si(001) vicinal surfaces, double-layer step edges are known to align regularly. The present calculations show a possibility to align CNTs using step edges as templates.

§3. Formation of Research Work

(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	Assistant Professor	H17.10~
	Daisuke Takahashi	University of Tsukuba	Assistant Professor	H17.10~
	Savas Berber	University of Tsukuba	Research Associate	H17.10~
	Jun-ichi Iwata	University of Tsukuba	Post-doctoral fellow	H17.10~
	Naoto Umezawa	University of Tsukuba	Post-doctoral fellow	H17.10~
	Katsumasa Kanaya	University of Tsukuba	Graduate student	H17.10~

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

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

① Number of Publications (0 papers in Domestic journals, 2 papers in International journals)

② Detailed Information of Thesis

- 1) K. Kamiya, M. Boero, K. Shiraishi and A. Oshiyama, "Enol-to-Keto Tautomerism of Peptide Groups", J. Phys. Chem. B **110** (2006) 4443.
- 2) S. Berber and A. Oshiyama, "Atomic and Electronic Structures of Carbon Nanotubes on Si(001) Stepped Surfaces", Phys. Rev. Lett. **96** (2006) 105505.

(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)