Nonadiabatic electron dynamics and many-body nuclear dynamics in molecules

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To understand the quantum effects of heavy particles (nuclei) in chemical reactions, it is necessary to track the wavepacket dynamics during the reaction. However, with the modern massive parallel computers, it is still prohibitive to perform a primitive fully-quantum wavepacket dynamics simulations, because the required amount of calculation grows exponentially with the number of degrees of freedom. To overcome such a situation, we have been continuing researches based on the action decomposed function (ADF) [1, 2].

In the theoretical framework of ADF, wavepacket dynamics is described in terms of an ensemble of classical trajectories. Starting from the fundamental equation of ADF, it is found that dynamics is decomposed into two terms. One is proved to represent geometrical change of small spatial region around the reference trajectory, and the other is the "diffusion operator" with a pure imaginary diffusion constant.

So far, our preliminary numerical studies have already shown that the geometrical change around the reference path is described well with the nearby running ones, and also that quantum effects are able to be well incorporated thereby. These facts provide a significant advantage for the calculations of real systems with many dimensions, because a reference trajectory is reused as a nearby for some other nearby paths.

Although we have not embarked on practical massive parallel computations based on this theory, we are going to make a start of many-body nuclear dynamics simulation, further proceeding to the connection to nonadiabatic electron dynamics. Numerical results successfully obtained for test systems are shown in Fig. 1.



Figure 1: ADF wavepacket height carried on a classical trajectory. (a) For a twodimensional system, it is confirmed that the ADF wavepacket component (blue) reproduces the fully-quantum result (red) very well. (b) ADF wavepacket calculation is applicable for a 100-dimensional test system.

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Density-Matrix Renormalization Group Study of Effective Spin Models for Na₂IrO₃

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The Kitaev-Heisenberg honeycomb lattice model has recently been proposed to describe magnetic properties in A_2 IrO₃ (A = Na, Li). The model includes an isotropic Heisenberg term and strongly anisotropic Kitaev terms. The Kitaev terms give a spin-liquid ground state. With increasing the strength of Heisenberg coupling, the ground state firstly turns into a stripy antiferromagnetic phase and then into a Néel antiferromagnet. The x-ray and neutron scattering experiments indicated that the ground state of Na₂IrO₃ is most likely characterized by a zig-zag spin structure. However, this type of magnetic order cannot be explained theoretically by the Kitaev-Heisenberg model. It is necessary to introduce further neighbor Heisenberg couplings and/or trigonal distortion of the oxygen octahedra.

In this project, we have studied extended Kitaev-Heisenberg models including these additional terms by using two-dimensional density-matrix renormalization group method (2D-DMRG). Firstly, we have included the second- and third-neighbor Heisenberg exchange interactions into the Kitaev-Heisenberg model and examined the ground-state phase diagram by calculating spin-spin correlation functions. From a previous classical-spin calculation of the model, it has been reported that there appears a zig-zag phase at a region where the second- and third-neighbor exchange interactions are large. Similarly, our 2D-DMRG calculations up to 6x6 lattice with both cylindrical and periodic boundary conditions have shown the presence of the zig-zag phase. Overall phase diagram including stripy and Néel phases is also consistent with the classical-spin calculation. However, such a large value of the long-range exchange interactions might be unrealistic for A_2 IrO₃.

We have also performed 2D-DMRG calculations for another extended Kitaev-Heisenberg mode proposed recently [1]. A zig-zag phase is found, being consistent with exactdiagonalization calculations [1]. This project is now in progress.

This works was done in collaboration with K. Shinjo and S. Sota.

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Possibility of deconfined criticality in SU(N)Heisenberg models at small N^*

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The regular Heisenberg model, i.e., the SU(2) symmetric quantum spin model can be easily generalized to the SU(N) symmetry for arbitrary N by replacing the Pauli spin operators by SU(N) generators. Thus we obtain SU(N) Heisenberg model. While the ground state of this model is the Néel state for N = 2, as is well-known, its nature at higher values of N had not been known until 1989 when Read and Sachdev predicted the valence-bond solid state as the ground state. The numerical confirmation of this prediction did not follow immediately. Absence of the magnetic order, and spontaneous braking of the lattice-rotational symmetry were confirmed more than ten years later. Even then, there was a remaining question concerning the nature the pattern of the singlet-pair covering of the lattice; whether it is columnar, plaquette, zigzag, etc. The distribution function of the dimerization order parameter was almost circular symmetric, making the question hard to answer. This was due to the proximity to the quantum transition point at which U(1) symmetry emerges. Concerning this model, there is another fundamental question regarding the nature of the quantum phase transition. While a field theory predicts a second order transition of a peculiar nature, a numerical study suggests the first order transition.

In the present study, we tried to solve this issue and carried out a series of quantum Monte Carlo simulations. We studied the SU(N) Heisenberg model with the four-body and six body interaction terms for the square lattice and the honeycomb lattice, respectively. The size of the system ranges from L = 8 to L = 256. For a limited size range, the finitesize scaling (FSS) works well and the resulting data collapse looked fine. However, we also discovered that depending upon the system sizes used in the FSS analysis, the resulting scaling exponents systematically drift. For example, the estimated exponent $y \equiv 1/\nu$ was $y \sim 1.5$ for L = 8, 12, 16, 24 whereas it was $y \sim 2.2$ for L = 96, 128, 192, 256, in the case of SU(3) model on the square lattice. The correlation decay exponent η_{ψ} was estimated as $\eta_{\psi} \sim 1.5$ for L = 8, 12, 16, 24 whereas it was $\eta_{\psi} \sim 1.2$ for L = 96, 128, 192, 256. From this observation, the apparent good scaling plots may not necessarily guarantee the 2nd order nature of the transition. On the other hand, if the transition is of the first order, the exponents should converge to $y \to 3$ and $\eta_{\psi} \to 0$, which are still far from what are actually observed in the numerical calculation.

Therefore, we must say that the true nature of the transition is still elusive and seems to demand even larger computation.

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Multi-scale simulation of nano-structured devices from electronic structures to mechanical properties

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In this fiscal year, we have treated two subjects. One is the Li-ion transfer mechanisms through the inteface between the solid-electrolyter interface (SEI) and liquid electrolyte in the Li-ion secondary battery (LIB) [1]. The other is the heat transfer mechanisims through the interface between the alumina-filler and polymer in a heat-dissipation material for high-power electronic devices [2].

The LIB is one of the most promising secondary batteries due to its higher energy density, high voltage, cycle performance, etc. The basic components of the electrolyte for the current LIB are ethylene carbonate (EC) for solvent and LiPF₆ for salt. The EC-based electrolytes are known to form a stable SEI on the graphite anode of the LIB in its first charging stage. The SEI transfers Li-ions but blocks electron current, and works to prevent further decomposition of the electrolyte. The SEI that is 10^{1} - 10^{2} nm in depth makes a major contribution to the overall resistivity in transferring Li-ions in the LIB. Despite the importance of the Li-ion transfer through the SEI, little is known about its microscopic Although detailed mechanisms. the composition of the SEI on the graphite anode depends on the settings and conditions of the electrolyte, the SEI is basically composed of inorganic solids (Li₂O, Li₂CO₃, LiF, etc.) and organic solids such as dilithium ethylene dicarbonate (Li_2EDC). The Li-ions are expected to diffuse through the relatively soft organic region.

We here investigate theoretically the microscopic mechanisms of the Li-ion transfer through the boundary between the SEI formed on the graphite anode and liquid electrolyte in the Li-ion battery [1]. A simulation system (about 2400 atoms) for the boundary is modeled using Li₂EDC, EC, and $LiPF_6$ for the SEI, solvent, and salt, respectively. After inserting Li-ions in the Li₂EDC region, we perform the first-principles molecular dynamics for simulation 4.8 ps using the

divide-and-conquer-type real-space grid DFT code (DC-RGDFT) [3]. Enhanced stability of the Li-ions at the boundary where EDC^{2-} and EC contact with each other is thereby found in the runs without salt, which acts to impede the Li-ion transfer through the boundary. It is also found that inclusion of 1.0 M LiPF₆ salt in the liquid EC weakens such impedance effect significantly. Physical reasons for those phenomena are explained in combination with separate DFT calculations (see, Fig. 1)



Fig. 1: (left) The snapshot at time 4.7 ps of the present DFT simulation run at 825 K. (right) The schemetic of the proposed mechanims for the enhancement of the Li-ion tranfer rate between the SEI and EC liquid due the LiPF₆ salt.

The integrated circuit (IC)-utilized modular packaging of electronic components for automobiles has advanced remarkably in recent years. It is beneficial to automobiles not only for their compactness but also for reliability and functionality. Such modular packaging has been essential particularly for the electric and plug-in hybrid automobiles. Further improvement of the packaging toward higher densities is therefore desired. One of the important techniques that should be realized in developing the higher-density

packaging is efficient dissipation of intense heat generated locally, e.g., in a power IC. Heat-dissipation material for that purpose in the forms of adhesive and bulking agent needs be soft to cover an IC without gaps. Composite systems of soft polymers and hard filler-particles (called fillers) are often used for such heat-dissipation materials. The fillers, which are about 1-10 micrometer in size, are made of the materials with higher thermal conductivities than the polymers for enhanced effective thermal conductivity of the heat-dissipation material. For its application to IC's, the heat-dissipation material should be electrically insulating. Automobile-parts companies have been putting great effort to design a novel heat-dissipation material with a few times higher thermal conductivity than the current ones under the conditions that it is electrically insulating, durable, and low cost.

We here address the enhancement mechanisms of the heat conductance of the polymer-filler interfaces by adding the surface-coupling agent in such a polymer composite material through through the non-equilibrium molecular dynamics (MD) simulation. A simulation system is composed of alpha-alumina as the filler, bisphenol-A epoxy molecules as the polymers, and model molecules for the surface-coupling agent. The inter-atomic potential between the alpha-alumina and surface-coupling molecule, which is essential in the present MD simulation, is constructed to reproduce the calculated energies with the electronic density-functional theory. Through the non-equilibrium MD simulation runs, we find that the thermal resistance at the interface decreases significantly by increasing either number or lengths of the surface-coupling molecules and that the effective thermal conductivity of the system approaches to the theoretical value corresponding to zero thermal-resistance at the interface. Detailed analyses about the atomic configurations and local temperatures around the interface are performed to identify heat-transfer routes through the interface (see, Fig. 2).



Fig. 2: Schematic of the atomic configuration of the present system with no surface-coupling molecule.

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Density Functional Study on Prediction of Electronic Properties of Nanostructures

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The aim of this project is to develop theoretical methodologies and computational techniques suitable for the current and future computer architectures, and apply thus obtained new schemes in order to clarify and predict properties of nanostructures on the basis of the quantum theory. The project is a part of research activities on "Nextgeneration Advanced Device Science" under Computational Materials Science Initiative (CMSI) conducted by MEXT, Japan. Currently four computational schemes are developed and tuned in this project: RSDFT (Real-Space Density-Functional-Theory) code, CONQUEST (Concurrent O(N)QUantum Electronic Simulation Technique) code, RSPACE (Real Space) code and RS-CPMD (Real Space Car-Parrinello Molecular Dynamics) code. The principal researchers to develop these four codes include Jun-ichi Iwata, Kazuyuki Uchida, Yasuteru Shigeta, Kenichi Koizumi and Shinnosuke Furuya for the RSDFT and RS-CPMD, Tsuyoshi Miyazaki, David Bowler for the CONQUEST, and Tomoya Ono for the RSPACE. We here report only a part of the achievements using RSDFT and RSPACE due to the limitation of the allotted length.

1. RSPACE: Electronic Structures and Magnetic Anisotropy Energies of Graphene with Adsorbed Transition-Metal Adatoms

Graphene has been one of the most promising candidates for future electronic and spintronic devices. Recent scanning tunneling microscopy experiment reported that it is possible to deposit single Fe, Co, or Ni adatom on graphene, tuning the electronic structures and realizing the spin texture of the graphene. The experiment pointed out that both the Fe and Co adatoms prefer an out-of-plane easy magnetization axis [1]. On the other hand, previous density functional theory studies suggested that the Co adatom exhibits an out-of-plane easy axis, whereas the Fe adatom exhibits an in-plane easy axis [2]. The number of theoretical studies is limited and do not provide sufficient results to discuss the problems in details. We study the electronic structures and magnetic anisotropy energies (MAEs) of graphene adsorbed with an Fe, Co, or Ni adatom in the presence of spin-orbit coupling (SOC).

The electronic band structures of graphene with adsorbed Fe, Co, and Ni adatoms in the absence of SOC are plotted in Fig. 1. The spin polarizations of Fe, Co, and Ni adatoms are 2.0, 1.0, and 0.0 μ_B , respectively. In the case of Ni adsorption, the Rashba effect is observed as a result of SOC with a **k**-dependent energy shift of π bands at the bottom of the Fermi surface (around -8.41 eV).



Figure 1: Band structures of graphene adsorbed with (a) Fe, (b) Co, and (c) Ni adatoms. The solid (dashed) curves indicates spin-up (spin-down) electronic bands. Zero energy is taken to be the Fermi level.

We found that the Fe adatom exhibits an inplane easy axis with an MAE of 1.6 meV, in contradiction with the experimental result, and the Co adatom shows an out-of-plane easy magnetization axis with an MAE of 5.6 meV, in agreement with the experimental observation [1]. For Co adsorption, the E_1 orbitals, which contain d_{xz} and d_{yz} orbitals, are occupied leading to the out-of-plane easy axis of the Co adatom. The E_1 orbitals are unoccupied in the case of Fe adsorption, resulting in an in-plane easy axis.



Figure 2: Fermi velocity normalized to the velocity of single layer graphene $v_{\rm F}^0$, as a function of θ . The velocities in the optimized structures $(v_{\rm F})$ and those for the flat structures with the interlayer distances of 3.61 Å $(v_{\rm F}^{\rm far})$ and 3.34 Å $(v_{\rm F}^{\rm near})$ are plotted.

2. RSDFT: Electron Localization due to Moiré Patterns in Twisted Bilayer Graphenes

Interference of two waves causes rich phenomena in nature. Beat patterns in sounds and Moiré patterns in sights are commonly recognized in human life. In condensed matter, two periodicities in atomic arrangements slightly different to each other induce a Moiré pattern: *e.g.*, turbostratic stacking of surface layers of graphite leads to a Moiré pattern which is observed by scanning tunneling microscope (STM). How electron waves sense Moiré patterns of atomic arrangements is an intriguing issue which has never been pursued before.

Bilayer graphene (BLG) is produced by exfoliation of graphite or by heat treatments of SiC surfaces. Typical stacking of the two layers is either AB (Bernal) or AA. However, the two graphene layers are often twisted to each other in their basal planes. The two layers with a tiny twist angle θ generate a Moiré pattern with its period $L = \sqrt{3}d/(2\sin\frac{\theta}{2})$, where d is the C-C bond length.

The first-principles electronic-structure calculations for such twisted bilayer graphene (tBLG) have been regarded formidable: Even if we confine ourselves to tBLGs where the Moiré period L is commensurate with the period of SLG, the number of atoms in a unit cell increases tremendously with decreasing θ , reaching tens of thousands for $\theta \leq 1^{\circ}$. We here apply our newly developed RSDFT code which has been optimized for current massively parallel multi-core supercomputers and enables us to perform the total-energy electronic-structure calculations for unprecedent-



Figure 3: The side and top views of the totalenergy optimized tBLG with the twist angle θ of (a) 29.4°, (b) 8.26°, and (c) 3.89°. In (b) and (c), the corrugation Δ is visible with the longest distance d_{far} and the shortest distance d_{near} . In (d), the distances d_{far} and d_{near} as functions of the twist angle θ are shown. The orange and blue circles in the top views in (b) and (c) depict the AA and AB stacking regions, respectively.

edly large systems consisting of 10 - 100 thousands atoms in the density-functional theory (DFT).

We have found that there is a critical twist angle $\theta_{\rm e} \sim 5^{\circ}$ from either the AA or the AB stacking, below which the Fermi velocity $v_{\rm F}$ decreases dramatically toward zero to cause flat bands at the Fermi level $E_{\rm F}$ [Fig.2]. This $v_{\rm F}$ reduction is a consequence of localization of electrons sensing the Moiré patterns in tBLGs. We have also found that the two graphene layers are corrugated below another critical angle $\theta_{\rm a} \sim 10^{\circ}$ [Fig.3]. The two critical angles $\theta_{\rm e}$ and $\theta_{\rm a}$ are *unequal* to each other, reflecting the difference in the sensitivity to the Moiré pattern between the electron waves near $E_{\rm F}$ and the valence-electron density in the honeycomb lattice which decides the atomic structure.

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Materials design for spintronics/multiferroics applications

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In this project, we have developed codes which enable the study of spintronics and multiferroics materials. We have developed a program code of newly parallelized density functional electronic structure calculations (CPVO). We also made a program that enables drawing spin textures by using numerical results which are calculated by using the OpenMX code (Fig. 1). This program is useful to analyze the results of fully-relativistic density functional theory calculations.

We study the electronic structures of ZnO which is a hopeful material for spintronics application. We analyze the lowest conduction band. We find the Rashba rotation near the conduction band bottom (Fig. 1). When the biaxial strain is introduced, the drection of the Rashba rotation can be reversed. We study the cases of tensile stress (ε_{xx} =4%) and compressive one (ε_{xx} =-4%).

To find the mechanism of the inversed Rashba effect, we calculate the electric polalization of the bulk ZnO. We find that the directions of the electric field in the cases of the tensile and compressive stresses are different (Fig. 2). This opposite direction of the electric field is the origin of the inversed Rashba effect. We expect that an effective spin filter is achieved by using the above mentioned inversed Rashba effect [1].

We also investigate the stable atomic structures of Tl-adsorbed surface of Tl/Si(111); Tl1/3/Tl/Si(111). For the system, the adsorbed Tl has four typical sites; T4, H3, bridge, and T1 models. After the atomic structure optimizations, the T4 model, in which there exist three nearest neighbors between the adsorbed and substrate Tl atoms, is found to be the most stable. According to our calculation, the bridge model is also comparably stable as the T4 model. The realistic surface configuration can be verified by experimental observation.

For the T4 model, the electronic structure is investigated. Fig, 3 shows the band dispersion curves in Tl1/3/Tl/Si(111) and those in Tl/Si(111) along the symmetry lines of 1st Brillouin zone. The dispersion curves which indicate folding characters of are Tl1/3/Tl/Si(111). The important result is that just below the Fermi level at K-bar point, there is the p-orbital component which comes from the Tl atoms in the 2nd layer of system. This means that the absorbed Tl atom provides electrons to the conduction band where the spin-polarization

is induced by the spin-orbit interaction in Tl atoms. This spin-polarization is found to be along the vertical direction of surface both in experimental and theoretical approaches [2]. These properties in the electronic structure may imply that such surface like Tl1/3/Tl/Si(111) is available for spintronics applications.

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 $\Delta \vec{P}(z) \vec{E}(z)$ $\Delta P(z) \bar{E}(z)$ 0.3 (b) 0.2 $\Delta \overline{P}\left(C/m^{2}\right)$ 0.1 0 -0.1 -0.2 -0.3 -4 -2 0 2 4 Strain (%)

 $(c_0/a_0), u_0$

 $(c/a) < (c_0/a_0), u > u_0$

 $(c/a) > (c_0/a_0), u < u_0$

(a)

Fig. 2: Electric polarization of ZnO.



Fig. 1: Lowest conduction bands and spin textures of ZnO.



Large-scale molecular dynamics calculation study of viruses

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In the initial stage of infection, virus is recognized by a receptor. This causes entry of the virus into the cell by endocytosis mechanism. Then, the virus is uncoated and releases the RNA. In this study, in order to investigate the interaction between the poliovirus capsid and the receptor, all-atom molecular dynamics (MD) simulation has been performed for the system consisting of poliovirus capsid, the receptor (CD155-D1D2 domain), and aqueous electrolyte solution. To our knowledge, this is the first calculation to investigate the virus infection at a molecular level by using MD calculations. Then, CHARMM force field with CMAP for proteins and TIP3P model for water are used. The fast multi-pole method (FMM) combined with Ewald method is used to evaluate long-ranged Coulomb interaction. The total number of atom in the box is over ten million (see Fig.1).

The distance r between the virus capsid and CD155-D1D2 was fixed at several r. The calculations have been performed using our highly parallelized general-purpose molecular dynamics simulation program for large-scale systems,,MODYLAS [1]. Then, the calculated mean forces and free energy profile of binding of the virus capsid to the receptor as a function of r between their centers of mass are obtained. The calculations showed that attraction interaction works between the virus capsid and the receptor in aqueous electrolyte solution in spite of the same negative sign of the total net charge of each capsid and receptor.



Fig.1 A snapshot of a poliovirus capsid particle (blue, red, and green represent VP1, VP2, and VP3 proteins) and D1 and D2 domains of the CD155 receptor (brown) in solution.

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Theoretical simulation of thermoelectric figure of merit ZT of organic composite materials and nanostructured materials

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In our group, non-equilibrium transport theories of electron and phonon have been studied and developed, some of which have been extended with first principle density functional methods. While the theory has been tested for some models representing nanostructured/molecular junctions, it has been applied for various channel materials including bulk thin films as well. In this FY, we have focused our attentions to thermoelectric properties of organic materials.

The basic start point of our theory comes from the previous theory treating electron and phonon currents including the coupling between them. [1-5] The low energy transport physics such like the local heating effect and the temperature dependent conductance has been discussed thereby. Based on this background, we studied organic thermoelectric materials in this FY. We have studied the problem without taking into account the electron-phonon coupling for simplicity, in order to make parallel discussions with the standard linear response theory familiar in the condensed matter physics textbooks, which do not include the coupling effect.

Firstly, we studied the general conditions requisite for large values of the thermoelectric figure of merit ZT.[6] We have used a single chain tight-binding model bridging the two semi-infinite electrodes defined on the cubic lattice and have explored various values of the energy gap $\Delta E = E_F$ - ε where E_F is the Fermi energy of the electrode and ε is the atomic site energy. Along with the figure of merit ZT, Z_eT which is defined by $ZT=Z_eT[1/(1+\kappa_{ph}/\kappa_e)]$ where κ_{ph} and κ_e represent phonon and electron heat conductance, was also examined. Z_eT gives the upper limit of ZT realized only when κ_{ph} is 0. The result summarized in Fig.1 indicates that ZT and Z_eT get enhanced when the Fermi energy comes close to the "band edge" of the single chain. Another important information is that ZT is largely reduced from Z_eT due to the finite value of κ_{ph} .

The formalism used for the model calculation has been converted to first principle methods. We have developed first principle density functional codes to calculate the phonon transport. Thermoelectric properties of molecular junctions with small single molecules and organometallic thin films have been investigated so far. In Fig.2., ZT of organometallic multilayers is shown. In this case only,[7] we simplified the phonon transport calculation using a rigid body approximation for the multilayer to reduce the computational cost for this system size. Because of the finite layer size effect, the Seebeck coefficient can change its sign as we increase temperature leading to the zero value of ZT at around T=220K in the case of the Ruthenium complex with the layer size L=3. We found a strong metallic atom dependence on the magnitude of ZT, however. Fully systematic first principle calculations of the phonon heat conductance and ZT have been made a lot for a series of single molecular junctions, which will be published soon as well as phonon-phonon scattering effects significant at high temperature.

Electric heat transported to the source (S) and the drain (D) electrodes were analyzed both theoretically and experimentally.[8] The nanoscale thermocouple integrated scanning tunneling probes (NTISTPs) were used for the experimental analysis. The asymmetry in the heat transported to the S and the D electrode denoted by Q_S and Q_D is found and is shown in terms of the $Q_S(V)$ vs $Q_{Total}(V)=Q_S(V)+Q_D(V)$ plot. In the case of symmetry, i.e., $Q_S(V)=Q_D(V)$ or $Q_{S,D}(V)=Q_{S,D}(-V)$, the slope of the plot should be 0.5. Deviations from 0.5 indicate the asymmetry, which depend on the bias voltage V. Both experimental and theoretical results indicate the asymmetry in quantitative agreement each other. The asymmetry comes from the electron-hole asymmetry and then depends on the sign of the Seebeck coefficient.

Not only for single molecular junction, but also for high-K hafnium oxide thin films exhibiting the resistive random access memory (ReRAM) behavior have been investigated in terms of the first principle transport calculations.[9,10] The success demonstrate that the usefulness of the theory for both academic and industrial researches.

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Energy gap dependence on ZT



Fig. 1. The energy gap (ΔE) and the temperature dependences on Z_eT and ZT. When E_F comes close to the "band edge", Z_eT and ZT get enhanced. ZT is largely reduced about by a factor of 1/20 due to the finite phonon heat conductance κ_{ph} .

First principle calculation of ZT

Organometallic molecular layer with Ru and Cu:L=1~3



Fig. 2. First principle calculation results of ZT for a class of organometallic multilayers. There clearly is a layer size (L) dependence. The result also depends strongly on central metals, i.e., larger value of ZT is obtained for Ru but not for Cu.



Fig. 3. Collaboration between first principle theory and experiment using the NTISTP shows asymmetry in electric heat transported to the electrodes, which well correlates with the sign of the Seebeck coefficient.

Large scale calculations on the fundamental processes of solar cells and their optimization in conversion efficiency and long lifetime

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<u>1. Density functional based molecular dynam</u> <u>ics study on redox potential of $Cu^{2+/+}$ and $I^{0/-}$ </u> in non-aqueous solution

The redox potential calculation using density functional based molecular dynamics simulation (DFT-MD) have been applied and revealed the changes of solvent coordinations of redox reaction in aqueous solution. The method is now applicable to directly compare experimentally observed redox potentials with the help of reference electrode calculation[1]. We establish the calculation method of redox potentials in non-aqueous solution, especially aprotic solvent for understanding and predicting the efficient organic synthesis and devices related electrochemistry because aqueous solution is mere one of solutions.

All the thermodynamic integral method were performed by using CP2K software package. The dummy / proton atom, $I^{0/-}$ or $Cu^{2+/1+}$ were immersed in 44 explicit acetonitrile molecules under periodic boundary condition. The side length of cubic unit cell is 15.74 Å and is determined to reproduce the experimentally observed density of AN solution (0.786 g cm⁻¹) for 45 AN molecules system. All quantum chemical calculations were performed with PBE functional, DZVP-MOLOPT-GTH basis set, Goedecker-Teter-Hutter type potential and 280 Ry for cutoff energy of the finest grid level under Gaussian and plane wave mixed basis method (QUICKSTEP). The MD simulations were performed for 6 ps after equilibrium to determine the constraint parameters of dummy atom and for 2.0 ps for each electronic state .

The calculated redox potential of $I^{0/-}$ and $Cu^{2+/+}$ in AN are in good agreement with experiments[2,3]. The redox potential calculated by using linear response is also good approximation for $I^{0/-}$ half reaction in AN because the solvation structure is almost same except for the range r < 4 Å. On the other hand, the radial distribution functions from Cu atom show that acetonitrile molecules strongly solvate both $Cu^{2+/+}$ ions. The solvation numbers of acetonitrile molecule for Cu^{2+} and Cu^+ are 5 and 4 in DFT-based MD simulation. This change of coordination number in AN is smaller than that in

aqueous solution but affects the redox potential to stray from linear response regime.

2. Theoretical investigations on the structure and the charge transfer state (CTS) of poly-3-hexyl thiophene / phenyl-C61-butyric acid methyl ester (PCBM/P3HT) as organic photovoltaic (OPV) cells

Recently, there are many studies about organic photovoltaic (OPV) cells that are expected to be used as energy conversion materials from the solar energy to electric energy. Because the OPV cells are thin-film, they are expected to be printed on various soft commodities Moreover, OPV can be made at low temperatures, about 420 K. So, OPVs enable to decrease the production cost. Up to present, many candidates to realize these features are introduced. Especially, PCBM/P3HT complex is thought as one of the most promising materials of OPV cells from the viewpoint of conversion efficiency. In this study, therefore, we investigated the structure of the interfaces of PCBM/P3HT complex and charge transfer states (CTs) that act as first key state in the course of energy conversion processes.

First, we obtained stable structures consisting of a few PCBMs and a P3HT with DFT-D method. Then, CTs of these structures are investigated with constrained DFT and timedependent DFT implemented. All calculations were carried NWChem code. In detail settings, B3LYP/6-31G* was used in the usual DFT and constrained DFT. CAM-B3LYP/6-31G* was used in the excited state calculation.

After we had investigated the stable structure and structural relaxation caused by the charge migration, we analyzed the lifetime of the CTs by the Marcus theory. From results of these calculations, we concluded that the lifetime of charge transfer state becomes longer by structural relaxation due to the charge migration. To make sure of this estimation, we investigated same calculation in interfaces of one PCBM and one MEH-PPV. As a result, we obtained the common feature.

3. Parallelization of a new open source software for excited state dynamics.

We are developing a new open source software for electronic-excited-state-dynamics based on semiempirical quantum calculations, which is named as MolDS[4]. Especially, The Molds aims to simulate electronic nonadiabatic dynamics in the energy conversion processes. By using the System C, the MolDS was hyperparallelized with openMP & MPI.

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Particle catalysis and nano-scale fluctuation

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Nano-particles have been attracting attention because of their enhanced activity, but its origin has not been well understood. The enhanced activity has often been attributed to the larger surface/bulk ratio and the existence of many steps and apexes, but here we point out that the solvent fluctuation plays an important role [1].

Effect of the solvent fluctuation was investigated using the first-principles molecular dynamics (FPMD) simulation combined with the effective screening medium (ESM) [2, 3]. The investigation was done first for a planar platinum/water interface, which was modeled using a slab geometry. The solvent fluctuation was found to affect the interface dipole and thus the interface potential drop, and importantly, the fluctuation of the potential was found to occur faithfully as expected from the Marcus theory. The theory is based on the simple argument on the polarization of the solvent, such that the electronic polarization is assumed to occur adiabatically and the geometric polarization occurs much slower causing therefore the fluctuation of potential.

The fluctuation is stronger as the surface area is made smaller relative to the thickness of the solvent. The situation corresponds to reducing the size of the particle; the fluctuation is enhanced more as the size is reduced.

The Marcus theory was then combined with the Butler-Volmer equation to see an effect on the exchange current, i.e., an index of the catalytic activity. The exchange current *i* was found to have a large size effect: *i* for a nanoparticle of diameter 3 nm is 15 times larger than that for infinite diameter (the bulk catalyst). This enhancement factor is indeed a large value which is comparable to (or larger than) the one achieved by the nano-shell method, i.e., a technique to enhance the activity by alloying the subsurface Pt. We expect the fluctuation effect as found here may be used to explain the known discrepancy between the experiments and existing theories.

In addition to this topic [1], we have also done several activities regarding the fuel-cell research. We have polished up the FPMD-ESM code to make the simulation more robust and efficient when run in the massively parallel supercomputers. Using this code, we have continued to study in detail the oxygen reduction (oxidation) reaction at the stepped Pt surface, which is considered as a key to identifying the reaction center of Pt. We have also done another activity to combine the simulation results with the most recent experimental data. By this hybrid theoretical and experimental study, we have excluded several important candidates for the oxygen reduction reaction pathways, thus considerably narrowing the possibility [4]. The ESM method has also been improved at the interface between the solution and the continuum region [3], so that the simulation can be robustly done at the constant potential conditions [5]. Establishing a microscopic theory for electrochemistry is a challenging theme, but to that aim, we have made important advances in this fiscal year.

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Massively Parallel Implementation of 3D-RISM Calculation with Volumetric 3D-FFT

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We have developed а new computational algorithm for solving the three-dimensional reference interaction model (3D-RISM) site theory for massively parallel machines and test it on the RIKEN K supercomputer and the supercomputer of the Institute for Solid State Physics, University of Tokyo.[1] The computational time and speedup of calculation the are improved by introducing the MPI/OpenMP hybrid parallelization with the volumetric 3D-FFT.[2] The program achieves good parallelization on hundreds of thousands of CPU cores with good scalability on the **RIKEN K** supercomputer.

To show the efficiency of the new program, the oligomerization process of the chymotrypsin inhibitor 2 in solution has been considered as a example. The massive parallel implementation realized the analysis for extra-large biological systems, because the numerous 3D-RISM calculations of each sampled monomer and oligomer structure with fine and large grid were required. Although our results of the analysis shown here were still preliminary, qualitative agreements with the previous calculations was observed, and the efficiency of the program was successfully demonstrated.

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All electron spectra and dynamics of functional materials from nanoclusters to crystals

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It is well known that local density approximation or generalized gradient approximation in density functional theory significantly underestimates the energy band gap. In contrast, GW approximation on the basis of many-body perturbation theory provides reliable results compared to hybrid method and is highly desirable. It is our aim to calculate XPS, UPS spectra, impurity levels, photoabsorption spectra, Auger spectra, and so on of molecules, clusters, and crystals such as TiO₂ by using allelectron GW approach and solving the Bethe– Salpeter equation systematically.

In this theme, we use our all-electron mixed basis code, TOMBO, which expresses quasiparticle wave functions as the linear combination of numerical atomic orbitals (AOs) and plane waves (PWs); see Figure 1. This is an unique and purely original first-principles program, which can describe all electrons from core to free electrons of both isolated and periodic (crystal) systems as complete eigenstates of quasiparticle Hamiltonian and enables us to calculate various spectra of electronic excited states by using GW approximation and solving the Bethe–Salpeter equation. The program is hybrid parallelized both with MPI and OpenMP. The parallel efficiency of the GW + Bethe–Salpeter part is excellent.

In this fiscal year, we ported in our latest crystal version of TOMBO (1) Conjugate gradient + RMM-DIIS + Davidson iterative diagonalization, (2) Broyden charge mixing, and (3) Broyden structural relaxation routines



Figure 1: All-electron mixed basis representation of quasiparticle wave functions.

from an earlier different simple-cubic version of TOMBO developed by Prof. Marcel Sluiter (Delft Univ. of Tech.) in our group. This was done by the support (supplementary budget) from CMSI. We also accelerated the code by introducing (4) Fitting of self-consistent potentials inside atomic spheres by means of the Chebyshev polynomial and (5) Approximate optimization of $3D \leftrightarrow 2D$ Fourier transformation for inclined unit cells. We have used System C (Fujitsu FX10) at the Institute for Solid State Physics of the University of Tokyo mainly for the debugging procedures and test runs of this new version of TOMBO in these implementations.

Already more than 18 years have past since the first development of the all-electron mixed basis code by ourselves, now the code is having variety of useful routines and still being improved. The LDA part of this latest version of TOMBO is planed to be open to the public, although the schedule is delayed because Ohno was hospitalized with illness during December 2013 to March 2014.

Direct molecular dynamics simulation of electrocaloric effect in ferroelectrics

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The electrocaloric effect (ECE) is an adiabatic change in the temperature, ΔT , of a material upon applying an external electric field. In particular, if an electric field is applied to a ferroelectric material at just above its phase transition temperature, $T_{\rm C}$, and the field is then removed, a large reduction in temperature is expected. It is widely believed that this effect is applicable to solid-state refrigeration.

Recent developments in the techniques of vapor deposition enable the production of defectfree single-crystal ferroelectric thin films. Such high-quality films allow for the application of large external electric fields, which cannot be applied to bulk polycrystalline specimens. Consequently, this advance in processing allows for investigation of the ECE in these ferroelectric thin films.

There have been several computational simulations of the ECE published in the literature. Ponomareva and Lisenkov have investigated the ECE of $Ba_{0.5}Sr_{0.5}TiO_3$ using Monte Carlo methods[1]. Rose and Cohen[2] have used molecular dynamics (MD) simulations and core-shell interatomic potentials to model the ECE in bulk LiNbO₃. Also using this form of atomic potential, Chen and Fang[3] have simulated the ECE in BaTiO₃ nanoparticles.

Here, we present a method to calculate the ECE directly by molecular dynamics simulations[4].

The effective Hamiltonian, constructed from first-principles calculations, and used in the present MD simulations is essentially the same as that in Refs. [5, 6]

$$H^{\text{eff}} = \frac{M^*_{\text{dipole}}}{2} \sum_{\boldsymbol{R},\alpha} \dot{u}^2_{\alpha}(\boldsymbol{R}) + \frac{M^*_{\text{acoustic}}}{2} \sum_{\boldsymbol{R},\alpha} \dot{w}^2_{\alpha}(\boldsymbol{R}) \\ + V^{\text{self}}(\{\boldsymbol{u}\}) + V^{\text{dpl}}(\{\boldsymbol{u}\}) + V^{\text{short}}(\{\boldsymbol{u}\}) \\ + V^{\text{elas, homo}}(\eta_1, \dots, \eta_6) + V^{\text{elas, inho}}(\{\boldsymbol{w}\}) \\ + V^{\text{coup, homo}}(\{\boldsymbol{u}\}, \eta_1, \dots, \eta_6) + V^{\text{coup, inho}}(\{\boldsymbol{u}\}, \{\boldsymbol{w}\}) \\ = Z^* \sum \boldsymbol{\mathcal{E}} \boldsymbol{w}(\boldsymbol{R}) \quad (1)$$

$$-Z^*\sum_{\boldsymbol{R}} \boldsymbol{\mathcal{E}} \cdot \boldsymbol{u}(\boldsymbol{R})$$
. (1)

The true atomic structure has properties determined by the complex chemical bonding between the atoms, but in the model system the complexity is reduced; the collective atomic motion is coarse-grained by local soft mode vectors, $\boldsymbol{u}(\boldsymbol{R})$, and local acoustic displacement vectors, $\boldsymbol{w}(\boldsymbol{R})$, of each unit cell located at \boldsymbol{R} in a simulation supercell. Each term in the Hamiltonian is described in Ref. [6].

The procedure to estimate ΔT involves two steps: first constant-temperature MD is performed for a fixed external electric field, \mathcal{E} , in the canonical ensemble using the velocityscaling thermostat. This allows the system to equilibriate. Next, the external electric field is switched off and the system is simultaneously changed to a constant-energy MD in the microcanonical ensemble that is allowed to evolve using the leapfrog method. The final state at the end of the constant-temperature MD is used as the initial state of the constant energy MD. All MD simulations are performed with our original feram software. feram is distributed freely under the GNU General Public License (GPL) and can be found at http://loto.sourceforge.net/feram/.



Figure 1: A comparison of the three MD methods to simulate the ECE. The temperature dependence of the ECE ΔT of BaTiO₃ is plotted versus ambient temperature for switching the applied external electric field from 160 to 60 kV/cm in the [001] direction.



Figure 2: The temperature dependence of ΔT for PbTiO₃. There is an ordinate for both the raw data ΔT and for the corrected data $\Delta T_{\text{corrected}} = \frac{2}{5}\Delta T$ that accounts for the underestimated specific heat capacity.

The ECE response is calculated using the *indirect* method[7], *direct MD* method, and *direct optimized* method and are compared in Fig. 1. The values of ΔT , corrected for the underestimated heat capacity in the *direct* methods, are also given in the figure. More detailed results are described in Ref. [4].

In Fig. 2, the temperature dependence for the ECE ΔT of PbTiO₃, under various initial external electric fields is compared.

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Structure Formation of Surfactant Membranes under Shear Flow

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We have been developing simulation of nonionic surfactant membrane assemblies to reveal the mechanism of formation of onion structures that have been observed in the experiments for more than 20 years[1]. To realize simulations of such multi-layered systems, a highly coarsegrained model is necessary. In this project, we adopt the meshless membrane model, forming a monolayer surface representing bilayer membranes exhibiting bending rigidity and other standard membrane properties. The size of each particle corresponds to the membrane thickness *i.e.* around 10 nanometers, and simulation of a large number of particles can represent a membrane system with many layers. I have simulated as many as one million membrane and solvent particles that can contain 30 layers of the membranes. Their rolling up instability has been found out in agreement with the experiment. Please see our invited article in this Activity Report and Refs. [2, 3] for details.

While we could successfully reproduce the instability experimentally observed on the course of onion formation, the nal onion structure could not be reproduced. One of the reasons can be attributed to the short of system size. In the experiments, diameters of the onion structures typically exceed 10 μ m, and thus, they are composed of at least 100 layers. To realize this order of system size, the simulation size should be made far larger to sub-billion particles scale, with the use of superparallel computers.

I have been continuing our e orts to develop our code, bringing optimization on the SPARC processors into view. The performance of our code has turned out to be less than 5%compared with the theoretical peak FLOPS at the bottleneck (*i.e.* force calculation part) on System C. Since optimization by the C++ compiler has turned out to be quite unreasonable, I have asked for consultation through CMSI in last September. The support sta has promised to work on improvement of the compiler to achieve the same performance as FORTRAN for standard two-body force calculation. Howevr, I have not received the result from them as of May 2014. Improvement on the performance of our code is still going on.

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Computational-Science Study of Frustrated Magnets

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It is well known that a quantum spin system is a typical many-body problem that is difficult to be investigated. Computational approaches are quite useful to study it. Among them, however, quantum Monte Carlo method faces with a so-called negative sign problem when a system includes frustrations in it. Density matrix renormalization group method is a powerful to a one-dimensional system; on the other hand, the application to systems in dimensions larger than one is now under developing. When one wants to study a two-dimensional frustrated magnet, therefore, numerical-diagonalization method is a reliable way although this method can treat only very small systems. Under circumstances, we developed an MPI-parallelized code of numerical diagonalizations based on the Lanczos algorithm[1]; thereby, we can treat systems that are as large as possible beyond limitations determined by computer resources when a user carries out calculations in a single node.



Figure 1: Cairo-pentagon lattice

The primary study of the present project is to clarify the behavior of the Heisenberg antiferromagnet on the Cairo-pentagon lattice^[2] by means of the Lanczos-diagonalization code mentioned in the above. The Cairo-pentagon lattice is illustrated in Fig. 1. A noticeable feature is that the lattice is composed of only pentagons although the pentagons are not regular polygons. There are two kinds of vertices in this lattice: one is the vertices with the coordination number z = 3 and the other is the vertices with z = 4. From the two kinds of vertices, the system includes two kinds of antiferromagnetic interactions. We study the magnetization process of this model when the ratio of the two interactions is tuned; we focus our attention on the behavior around $m/m_{\rm s} = 1/3$, where m and m_s denote the magnetization and its saturation, respectively. We find that a magnetization plateau appears at $m/m_{\rm s} = 1/3$ and that there exist two regions where the states at $m/m_{\rm s} = 1/3$ show properties that are different from each other. The boundary between the two regions is about 0.78. We clarify that the plateau is accompanied by a magnetization jump on one side among the edges and that which side the jump appears depends on the ratio. The behavior is related to the occurrence of the spin-flop phenomenon, which is similar to the case of the Heisenberg antiferromagnet on the square-kagome lattice[3].

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First-principles electronic structure calculation of permanent magnets using the screened KKR Green's function method

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The KKR Green's function method is a method for first-principles electronic structure calculations. In this method, instead of solving eigenvalue problems as in most of band calculation codes, Green's function of the Kohn-Sham equation is directly calculated. By taking the imaginary part of the Green's function, we can obtain the electron density very accurately and efficiently.

The Green's function is calculated from that of an arbitrary reference system by solving the Dyson-type equation. In the process of solving the Dyson equation, inversions of matrices of a dimension proportional to N (N: the number of atoms in a unit-cell) is required. In the usual KKR method, the free space is chosen as the reference system. When N becomes large, the computational cost increases drastically. This is because $O(N^3)$ operations are required to invert a $N \times N$ matrix. To overcome this difficulty, the concept of screened KKR was proposed. In the screened KKR method, a system with repulsive muffin-tin potentials of a constant height is chosen as the reference system. In this reference system, the Green's function decays exponentially in real-space if the energy range is sufficiently lower than the repulsive potential height. Then we can ignore long range propagations without sacrificing the accuracy. In this case, the matrix that we must invert becomes sparse. Therefore, one can expect large improvement of the calculational efficiency by use of an efficient sparse matrix solver. This technique has been mainly applied to the multilayered systems which extend to only one dimensional direction assuming twodimensional periodicity. For such systems, the

matrix becomes block tridiagonal and the computational cost is exactly proportional to the layer thickness.

It is desirable to apply the screened KKR technique to more general and complex systems which extend to all three dimensional directions. For such general large super-cells, we must treat general non-Hermitian block sparse matrices. As a sparse matrix solver, the iterative method, which is often used to solve linear simultaneous equations with sparse coefficient matrices, is more efficient than the direct method such as the LU-factorization. This algorithm is also suitable for the parallel computing.

We developed a full-potential based screened KKR code which can treat such large supercells by combining the iterative method for solving the Dyson equation with parallel computing techniques [?]. Through the test calculations, it was shown that our code is reliable and well parallelized w.r.t the number of atoms in the super-cell. we also confirmed that our code runs on the FX10 computer without any trouble. By the use of our code, it is possible to execute the all-electron level first-principles electronic structure calculations for super-cells which include thousands of atoms within a reasonable time. Our code should be useful for our research project: Elements Strategy Initiative Center for Magnetic Materials(ESICMM).

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Ordering in frustrated spin systems

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Several two-dimensional frustrated Heisenberg spin systems have a topologically stable point defect, a Z_2 vortex. About 30 years ago it was proposed that a thermodynamic phase transition driven by binding-unbinding of the Z_2 vortices occurred at a finite temperature $T = T_v$ [1]. In constast to the case of the Kosterliz-Thoulses transion in two dimensional XY spin systems, the Z_2 vortex transition occurs keeping the spin correlation length finite.

The ordering of Z_2 -vortices has been studied mainly on the triangular lattice Heisenberg AF. Although recent Monte Carlo simulation up to L = 1536 has suggested the occurrence of Z_2 vortex transition at a finite temperature, the existence of "true" phase transition has not been resolved because the spin correlation length at the estimated transition temperature was longer than the system size. In order to clarify the nature of the Z_2 vortex transition through numerical simulations, we need larger system beyond the spin correlation length.

In order to perform larger scale Monte Carlo simulation, we consider an effective *non-frustrated* SO(3) model of two-dimensional frustrated Heisenberg magnets. The Hamiltonian of the model is give by

$$\mathcal{H} = -\frac{J}{4} \sum_{\langle i,j \rangle} \operatorname{Tr} R_i R_j^t \qquad (J > 0), \quad (1)$$

where R_i is a SO(3) rotation matrix on the site i, and $\sum_{\langle i,j \rangle}$ means the sum over the nearestneighbor pairs. Although this effective model does not have frustrated interactions, it has a topological Z_2 vortex similar to the frustrated magnets.

We have implemented parallelized Wolff-Swendsen-Wang type cluster algorithm and parformed an extensive Monte Carlo simulation of the model. The lattice is a $L \times L$ square lattice with periodic boundary conditions. By extrapolating an characteristic temperatures of the volticitly modulus to the thermodynamic limit, we estimate the Z_2 vortex transition temperature as $T_v/J \simeq 0.275$. However, because the spin correlation length at T_v is estimated about from 5000 to 10000 lattice spacings, the present system size L = 4096is too small to conclude the presence of true phase transition. In order to have the conclusive evidence of the Z_2 vortex transition, we need larger system such as L = 8192 or L = 16384.

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Search for New Structures and Functions of Nano-sized Molecules

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Recent super computers consist of a huge number of CPU cores and nodes, and high performance parallel algorithms and programs are necessary to use such computers efficiently. The development of a new quantum chemistry program started with MPI and OpenMP for inter- and intra-node parallelization in 2012. Geometry optimization calculations are significant to analyze and predict molecular structures and functions. Therefore, a parallel program for energy gradient calculations is developed in this study.

Based on the parallel algorithm [1] for Hartree-Fock energy calculations, an MPI/OpenMP parallel algorithm for DFT

!\$OMP parallel do reduction(+:gradient)
do µ=n, 1, -1 < Distribution by OpenMP
do ν=1, μ
λ start=mod(μ *(μ +1)/2+ ν +mpi_rank,nproc)+1
do λ = λ start, μ ,nproc < Distribution by MPI
do $\sigma=1, \lambda$
Calculation of derivative of 2e-integrals
$(\mu\nu \lambda\sigma)$ +Add them into gradient array
enddo
enddo
enddo
enddo
call mpi_allreduce(gradient)

Fig. 1: Parallel Algorithm for Derivative Terms of Two-Electron Integrals.

energy gradient calculations is developed. The calculation for the derivative terms of twoelectron integrals is the most time-consuming step, and the algorithm is shown in Fig. 1.

CPU and parallel performances of the program were analyzed with FUJITSU FX10 and its profiler. The source codes were modified according to the profiler data.

DFT energy gradient calculations were performed on the K Computer with $C_{150}H_{30}$ (cc-pVDZ basis, 2250 functions). The speedup is almost linear even on 16384 CPU cores as shown in Table 1. It is now practical to calculate geometries and functions of nanosized molecules.

Table 1: Elapsed Time (sec) and Speed-up (in

parentheses) for DFT Energy Gradient Terms.

# of Cores	1024	8192	16384
One-electron	60.0	7.9	4.2
term	(1024.0)	(7777.2)	(14628.6)
Two-electron	342.0	42.9	21.3
term	(1024.0)	(8163.4)	(16441.7)
Total	402.0	50.8	25.5
	(1024.0)	(8103.3)	(16143.1)

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