3.5 CMSI projects

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 reactions. However, even with the modern massive parallel computers, it is still prohibitive to perform a primitive fully-quantum wavepacket dynamics simulations, because the required amout 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 linear fundamental equation of ADF, it is found that dynamics is decomposed into two terms. One is proved to represent geometry of small spatial region around the reference trajectory, and the other is the “diffusion operator” with a pure imaginary diffusion constant.

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.

Besides the advantage of describing multidimensional wavepacket dynamics, because of its structure, ADF theory also possesses an ability to reveal the quantum-classical correspondence in detail. Our previous study has made it clear that energy quantization is performed with action integrals and the so-called Maslov phases in the semiclassical regime [3]. However, such semiclassical phase quantization can yield a small deviation in the energy values, which becomes non-negligible when the Planck constant is large. We have performed many trajectory calculations to construct quasi-correlation function, leading to the quantized energies for multidimensional chaotic systems. Analyses of them via the ADF are now underway to lead to both more accurate description of energy quantization and better understanding of the role of the quantum phase in the wavepacket dynamics.

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Density-matrix renormalization group study of the extended Kitaev-Heisenberg model

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The Kitaev-Heisenberg (KH) honeycomb lattice model has recently been proposed to describe magnetic properties in A_2IrO$_3$ (A= Na, Li). The model includes an isotropic Heisenberg term and strongly anisotropic Kitaev terms. However, it has turned out that the KH model cannot straightforwardly explain a zigzag-type antiferromagnetic order observed in Na$_2$IrO$_3$. This discrepancy has inspired further studies about more suitable effective spin models for Na$_2$IrO$_3$. For example, anisotropic interactions due to trigonal distortions [1] have been introduced to the KH model to explain the zigzag order.

Motivated by these previous studies, we examine an extended KH model including such anisotropic interactions by using two-dimensional density-matrix renormalization group method (2D-DMRG) [2]. The 2D-DMRG calculations are carried out under periodic boundary conditions. We mainly use a system with 6 (along the y axis) × 8 (along the x axis) sites, i.e., a 48-site system. To perform 2D-DMRG, we construct a snakelike one-dimensional chain by combining the eight zigzag lines along the y axis, leading to a spin chain with long-range interactions. We keep 1000 states in the DMRG block and performed more than 10 sweeps, resulting in a typical truncation error 5×10^{-6} or smaller.

We make a phase diagram of the extended KH model around the Kitaev spin-liquid phase from the ground-state energy and spin-spin correlation functions [2]. Furthermore, we investigate entanglement entropy (EE) and the entanglement spectrum (ES). We find that the lowest level of ES at magnetically ordered states is nondegenerate. This is clearly in contrast to the Kitaev spin-liquid state, where all of ES form pairs. Such a degenerate structure in the Kitaev spin liquid is due to its gauge structure coming from its topological nature, and it depends on the boundary conditions. As a result, the Schmidt gap defined as the energy difference between the lowest and first excited ES changes at the phase boundary between the Kitaev spin liquid and other magnetically ordered phases. However, we find that the Schmidt gap cannot be a good measure of the phase transition between magnetically ordered phases.

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Study of Novel Quantum Phases and Critical Phenomena by Monte Carlo Method and Tensor Network *

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The objective of our group --- the QMC-TN collaboration in CMSI --- is to clarify the novel quantum phase transitions and phases using a massively parallel computation. Our list of specific targets includes (1) to clarify the existence/absence of the novel phase transition called deconfined critical point in the SU(N) Heisenberg model, and (2) to obtain quantitatively accurate phase diagram of spin-orbit Ir-compounds using the new numerical technique based on the tensor network variational wave functions.

As for the first target, in SY2014, we carried out a large-scale quantum Monte Carlo on the system C of ISSP for the SU(N) J-Q model at finite temperature. Because of the spontaneously broken discrete symmetry in the VBS phase at zero-temperature, in the VBS region, we are allowed to have a phase transition at finite temperature without violating the Mermin-Wagner theorem. Our calculation [1] revealed that this is indeed the case. We also studied the universality class of this finite-temperature phase transition to find that it is consistent with the Ashkin-Teller type transition for the square lattice and the 3-state Potts model for the honeycomb lattice. This is in consistent with the natural expectation since the Z4 symmetry and the Z3 symmetry are broken in these two cases respectively. Particularly interesting was that the critical index ν seems to diverge as we approach the quantum critical point of the square lattice model.

As for the phase diagram of the Iridium-based compounds, we developed an original computer program based on the PEPS wave function and the corner-transfer-matrix renormalization technique for the network contraction. Applying this program, we succeeded in obtaining the phase diagram of the effective model obtained through the first-principles calculation. [2]

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* This work is done in collaboration with Tsuyoshi Okubo and other members of the QMC-TN/CMSI collaboration.

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

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In the fiscal year of 2014, we have mainly treated two subjects. One is the hybrid quantum-classical (QM-CL) simulation study of the thermal diffusion of correlated Li-ions in graphite. The other is the rigid-body moleculular dynamics study of the quasi-liquid layer of sub-micrometer-scale Ice.

Diffusion of Li-ions in graphite is an essential elementary process in the current lithium-ion battery. The C-layers of graphite deform with Li due to relatively large size of Li-ion, which acts to confine the Li-ions and thereby create correlation between them. We address theoretically the thermal diffusivity of such correlated Li-ions in graphite by the hybrid quantum-classical simulation method. In this method, the quantum-region composed of the Li-ions and surrounding C atoms is treated by the density-functional theory, while it is embedded dynamically in the total system described with an empirical inter-atomic interaction potential. We thereby take into account the long-ranged deformation field in graphite in simulating the Li-ion dynamics.

Two kinds of settings of Li-ions are considered for the simulation runs at temperature 443K: (i) seven Li-ions are inserted in the same inter-layer space of the C-layers to study their intra-plane correlation, and (ii) additional seven Li-ions are inserted in the neighboring space (i.e., fourteen Li-ions totally) to study their inter-plane correlation. As for (i) depicted in Fig. 1, the Li-ions, concentrated initially with inter-ion distances of 2.5-4.2 Å, scatter due to their mutual Coulomb repulsion. After about 1ps, the Li-ions and surrounding C atoms thermalize well with deformed C-layers creating a cage for Li-ions, the radius of which is estimated about 13.5Å from present simulation runs. Diffusivity of Li-ions inside the cage is much higher than that of the cage itself. The long-time diffusion constant of the cage is the same order as that of an isolated Li-ion in graphite.

As for (ii), the Li-ions, concentrated initially in the higher and lower inter-layer spaces of the C-layer, firstly form domains, and then the domains repel each other horizontally. The result is in accord with the experimental finding that the Li-rich and Li-poor planes stack in an alternating sequence in graphite [1].

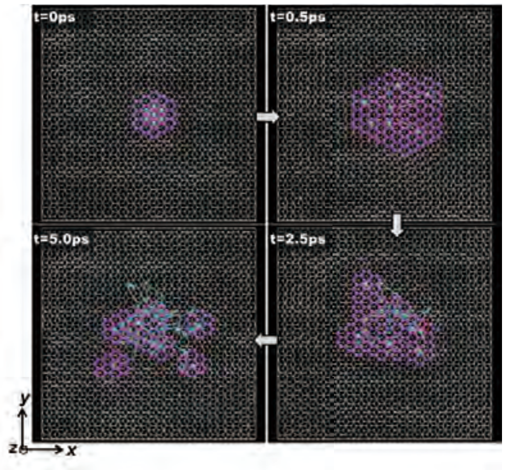

Fig. 1: The snapshots in a hybrid QM-CL simulation run. Cyan and magenta spheres are Li-ions and QM-C atoms, respectively. Gray spheres are CL-C atoms. Cyan curves are the trajectories of Li-ions.

The molecular dynamic simulation of a faceted ice-Ih crystal with the largest dimension of 0.06μm in a vacuum is performed by employing the TIP4P intermolecular potential at temperatures T_m - 23 K, T_m-13K, and T_m -1 K, where T_m is the melting point of the TIP4P bulk ice. The settings are depicted in Fig. 2. We thereby observe at all the temperatures that the quasi-liquid layers (QLLs) formed on the basal (0001) surfaces are bumpy and that the liquid bumps repeatedly form and break at various places in a random manner. At T_m -1 K, a liquid sheet appears under the liquid bumps. As explained in Fig. 3, at an intermediate temperature for the bilayer-by-bilayer surface melting, the molecules under the local areas of either thin or thick QLLs have respectively the tendency to melt or recrystallize [2].

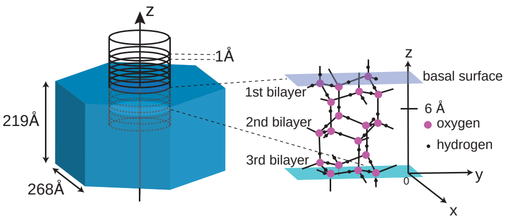

Fig. 2: Ice-Ih crystal in a hexagonal prism shape composed of 1,317,600 H_2O molecules (61 bilayers 21,600 molecules). The z-axis is perpendicular to the basal (0001) surface. We set z=0 at the bottom of the third bilayer from the outside. The radius of the virtual cylinder used for analyses is 114 Å.

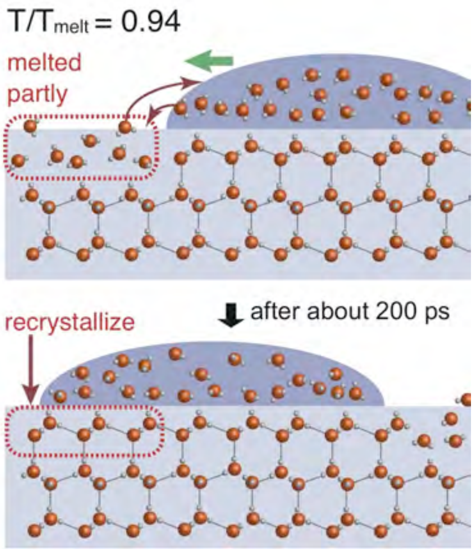

Fig. 3: Shemetic views of the dynamics of the quasi-liquid layer (QLL) of ice.

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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 make a program that enables drawing spin textures by using numerical results which are calculated by using the OpenMX code. This program is useful to analyze the results of fully-reletivistic density functional theory calculations.

We have performed the first-principles density functional calculation for the slab systems; single interface MgO/Fe, magnetic junction Fe/MgO/Fe, the double interface MgO/Fe/MgO, and Fe/TiO_2/SrO/TiO_2 [1]. To clarify the origin of electric field (EF) effect on the magnetic anisotropy energy from the interface, we discussed the electronic structure of interface Fe atom with using the calculated results. The partial density of states projected to the Fe atom at interface was calculated, for example, as shown in Fig. 1. In these PDOSs, the minority spin states of 3d orbitals are located around the Fermi level (E_F). Particularly, the angular orbitals except 3d($3z^2$-r^2) tends to have a peak on or above E_F. This is because these orbitals have no tight covalent bond within plane or to the interface. It was speculated that the important point was a non-linear behavior with respect to in-plane lattice constant. The energy location of Fe 3d (minority spin) states is raised when the lattice constant decreases due to an Fe-Fe orbital hybridization. However, as shown in Fig. 1, the location was lowered at a range of lattice constants. This may be ascribed to an entanglement among the orbital hybridizations of Fe and O atoms and electron exchange-correlations. By solving this entanglement, we could give a plausible explanation to the result about EF effects on MAE. To this end, systematic parallel computation, for example, of a set of many in-plane lattice constants, accelerates or allows us to draw an important insight for magnetic materials in electron junction devises.

We also study the spintronics application of ZnO. Recently, the physical properties induced by spin-orbit coupling (SOC) attract much wide scientific interests because of their applications to the spintronics. Spin textures induced by SOC has been extensively studied because they are crucially important to induce useful physical properties. The spin textures of persistent spin helix (PSH) has been investigated because it enables long spin life time, and thus new spintronics devices are expected to be achieved. Thus far, PSH has been studied only for zinc-blende semiconductors. We in the first time find that the PSH can be achieved for the wurtzite semiconductors.

We perform fully relativistic first-principles calculation on ZnO (10-10) surface and find the PSH spin textures (Fig. 2). These spin textures are well explained based on a simple spin-orbit Hamiltonian. The calculated values of the spin-orbit strength is comparable with those observed for various zinc-blende quantum well structures. Furthermore, the wavelength of the PSH is much small and thus the miniaturization of device can be achieved. Therefore, this study opens the gateway into the application of wurtzite structure semiconductors to the PSH spintronics.

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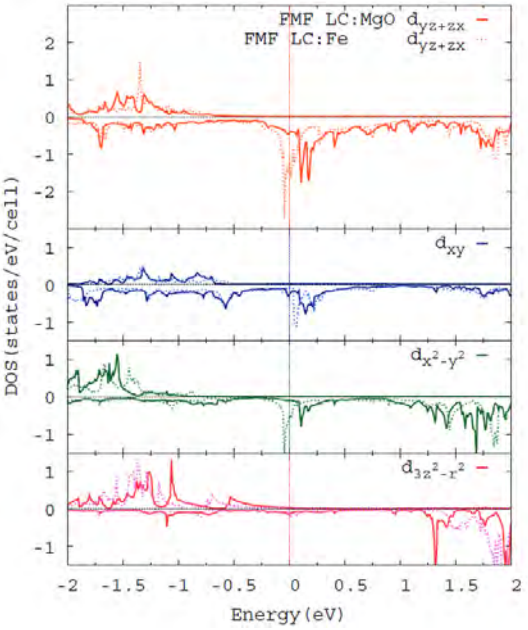

Fig 1. Partial density of states (PDOS) on the Fe atom at interface. The full and dotted curves specify large (bulk MgO) and small (bulk Fe) in-plane lattice constants, respectively.

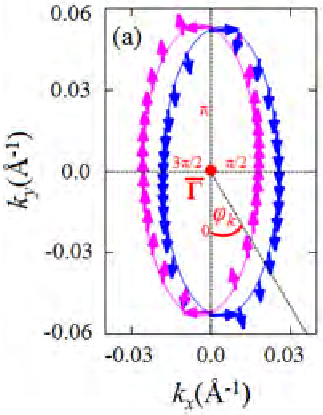

Fig. 2 Spin texture of the ZnO(10-10) slab. The z axis is in the (10-10) axis.

Large-scale molecular dynamics calculation study of viruses

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Polio virus capsids are composed of 240 proteins. The diameter is about 30 nm. The system may be constructed in computer by about 6.5-10 million atoms including solvent electrolyte solution. The K-computer is capable of executing MD calculation of this very large system. In a series of this study, calculations have been performed focusing our attention on the stability of the capsids[1]. Then, we extended our calculations to the initial process of infection, i.e. recognition of the capsid by a receptor. In order to investigate the interaction between the poliovirus capsid and the receptor, all-atomistic MD calculations have been performed for the system consisting of a poliovirus capsid and a receptor (CD155-D1) in aqueous electrolyte solution (see Fig. 1).

Last year, we showed attractive interactions found 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. This is the first calculation investigating virus infection at a molecular level based on the all-atomistic MD calculations. However, statistics was rather small such that we couldn’t reach a conclusion that the attraction works between the virus and receptor.

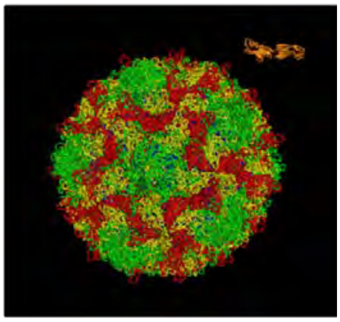

Fig.1 A poliovirus capsid and D1 domain of CD155 receptor in solution. Solvent molecules and ions are not drawn in the figure.

This year, we continued our calculations in order to obtain sufficient statistics to make a conclusion. Statistics of force more than ten times greater than before has been obtained. Based on the calculations, we concluded that the attractive forces do work between the capsid and receptor.

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

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1. Density functional based molecular dynamics study on redox potential of $Cu^{2+/+}$ and $I^{0/-}$ 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. 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 methods were performed with CP2K package. The dummy / proton atom, $I^{0/-}$ or $Cu^{2+/1+}$ were immersed in 44 explicit acetonitrile (AN) molecules under periodic boundary condition. The length of unit cell is set to 15.74 Å to reproduce experimental densities. 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 initial equilibration.

The calculated redox potential of $I^{0/-}$ and $Cu^{2+/+}$ in AN are in good agreement with experiments. The redox potential estimated with linear response is also good approximation for $I^{0/-}$ half reaction in AN because the solvation structure is almost same except for $r < 4$ 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 our DFT-MD simulations. 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. Large scale calculations of electronic excited states of molecular aggregates

We are, recently, developing software for molecular dynamics, which is based on quantum chemical calculation, on multiple electronic excited states including nonadiabatic effects because photocurrent conversions in organic solar cells take place on the electronic excited states. To do so, we optimized our software to run on the FX10 and K-computer with openMP/MPI hybrid parallelization technique. In detail, load balances between Hartree Fock for the ground state and configurational interaction for excited states are tuned. As a result, our code could obtain strong scalability (more than 10,000 cores) for the calculation of electronic excited states.

Efficient Implementation of 3D-RISM Theory to the FMO Method, and Its Applications

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An efficient implementation of the three-dimensional reference interaction site model (3D-RISM) theory to the fragment molecular orbital (FMO) method was proposed.[1] The method is referred to as FMO/3D-RISM method. The method allows us to treat an electronic structure of whole part of macromolecules, such as protein, as well as a solvent distribution around the solute macromolecules. The electrostatic potential should be calculated on grid point in the three-dimensional real space witch is used in 3D-RISM theory. Therefore, the reducing the computational cost to calculate the electrostatic potential is most serious concern.

In this article, we propose a procedure to save the computational cost for calculating the electrostatic potential in the framework of FMO method. The strategy of this procedure is to evaluate the electrostatic potential and the solvated Fock matrix in different ways, depending on the distance between solute and solvent. In the vicinity of solute molecule, the electrostatic potential is evaluated directly by integrating the molecular orbitals of monomer fragments of solute molecule, whereas that is described as the superposition of multipole interactions by using Taylor expansion of the electronic distribution of monomer fragment. The results are compared with those from the other methods. We apply the FMO/3D-RISM method to investigate the selective binding of cellulose by cellulose binding module (CBM).

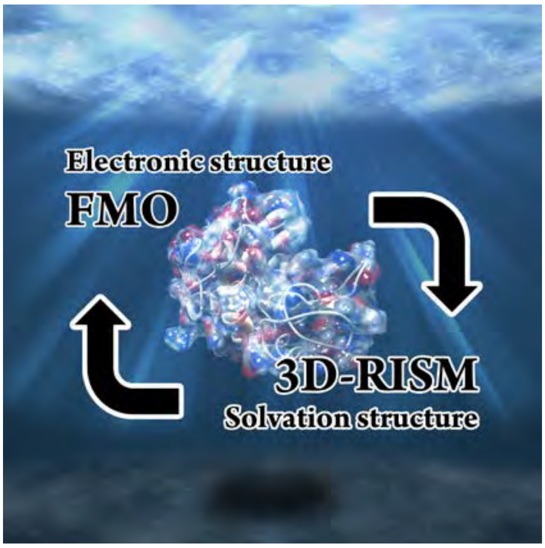

Figure 1: Schematic description of FMO/3D-RISM scheme.

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Fluctuation and surface tension on membrane surface

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Bilayer membranes can be treated as two-dimensional sheets. They form various forms, for example, vesicles, stomatocytes, and so on owing to its surface elasticity. The energy functional can be written in terms of mean bending curvature $H = c_1 + c_2$ as

$$\mathcal{H} = \sigma A + \int dA \frac{\kappa}{2} H^2, \qquad (1)$$

where σ represents the surface tension, A is the real area of the membrane. Based on this model, we have recently been performing large-scale simulation of structure formation in surfactant membranes. Recent topic include in my project includes large-scale deformation of multilamellar membranes under shear flow induced by implanted screw dislocations, which is ongoing at present.

This year, as a related problem, we are working on "residual tension" on a fluctuating membrane area. The area can be defined either as a real area or as the area of a projected area, which is two-dimensional area by projecting the membrane area onto an arbitrary plane. The surface tension σ is a quantity that is conjugate to the real area.

If we stretch a membrane surface, the surface area gets extended because of both the stretching of the actual surface and the suppression of fluctuations. The suppressed fluctuation leads to change in the projected area A_p, and therefore, there can be another definition of surface tension, which is called the "frame tension" in the literature. σ is the other tension which is specifically named "internal tension". We employ Monte-Carlo simulation on a lattice model of surfactant membrane, in an stress-controlled extended ensemble. On the membrane surface, we can control both the two tensions *i.e.* frame and internal tensions, and A and A_p assumes certain values in accord with these tensions. Whether or not these tensions agrees with each other has been an target issue of discussions for a long time. We have proven using the simulations that the difference between these tension should remain in the thermodynamic limit, and investigated their relation to the effective surface tensions reflecting the cutoff frequency (usually given by the molecular length unit providing the highest cutoff frequency.), on which we are now writing the paper draft[1].

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Computational-Science Study of Frustrated Magnets

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Since a quantum spin system is a typical many-body problem, it is difficult to study such systems generally. For the study, computational approaches therefore are quite useful. However, each method has not only merits but also demerits. Quantum Monte Carlo method can treat large systems but faces with a so-called negative sign problem when a system includes frustrations in it. Density matrix renormalization group (DMRG) method can treat systems when they are frustrated but this method is a powerful to a one-dimensional system. The application of this method to systems in dimensions larger than one is now under developing. On the other hand, numerical-diagonalization method is a reliable way irrespect of the point whether or not a system of target magnet is frustrated and irrespect of spational shape of the system. The largest weak point of this method is that 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]. This code can treat systems with its sizes that are larger than those determined by computer resources when calculations are carried out in a single node.

The primary study of the present project is to clarify the behavior of the magnetization process of the Heisenberg antiferromagnet on the kagome lattice by means of the Lanczos-diagonalization code mentioned in the above[2]. The magnetization process was originally studied in Ref. 3, in which the existence of the magnetization plateau was pointed out at one-third of the height of the saturation. The plateau was detected in the DMRG calculation with a help of sign-squared deformation in Ref. 4 which reported that a unique and particular quantum state with the nine-site structure is realized at the plateau. If such a unique state is realized, the critical behavior just outside the plateau is determined by the parabolic dispersion; thus the critical exponent δ is supposed to be unity. It was, however, clarified that the critical behavior around the height is different from the conventional one that is widely observed in two-dimensional magnets[5, 6]. Under this controvertial situation, we tackle to obtain a numerical-diagonalization result of the magnetization process of this model with a size that has not been reached before. We successfully calculate the result for a 42-site system by the use of the K computer. This size is the *world record* among all the cases irrespect to lattice structure of the $S = 1/2$ spin models to the best of our knowledge. The additional and novel result provides us with a more precise estimate of the critical exponents that are different from the conventional $\delta = 1$. Our study furthermore the case when the lattice is distorted in the $\sqrt{3}$ $\sqrt{3}$ type. Under controll of the distortion, our result indicates that the undistorted kagome point is just on the boundary between the ferrimagnetic state and the state proposed in Ref. 4. This indication suggests that the state with the nine-site structure as the long-range order is no longer stable at the undistorted kagome point.

Our result of a quantum spin system by large-scale parallelized calculations of Lanczos diagonalization make the true behavior of the system that other methods failed to detect. Our study suggests that large-scale Lanczos diagonalizations continue to contribute much to our understandings of these systems.

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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 that 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, which results in the matrix that we should invert being sparse. Therefore, one can expect a substantial improvement of the calculational efficiency through the 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 two-dimensional periodicity. For such systems, the matrix becomes block tridiagonal and the computational cost is exactly proportional to the thickness of layer.

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 super-cells by combining the iterative method for solving the Dyson equation with parallel computing techniques [1]. Through the test calculations, it has been shown that our code is reliable and well parallelized w.r.t the number of atoms in the super-cell, also confirming 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 calculations for super-cells which include thousands of atoms within a reasonable time. We also implemented the routines to calculate the effective magnetic exchange interactions *ab-initio*, which is very useful for studying permanent magnetic materials.

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Ordering of topological excitations of the frustrated magnets

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In several two-dimensional frustrated Heisenberg spin systems, a topologically stable point defect, a Z_2 vortex, plays an important role for ordering. About 30 years ago, a possible topological phase transition driven by Z_2-vortex binding-unbinding was proposed [1]. The remarkable feature of the Z_2-vortex transition is that the spin correlation length keeps finite at the transition temperature $T = T_v$. It is a sharp contrast to the Kosterlitz-Thouless transition, where the spin correlation length diverges below the transition temperature.

The nature of the possible Z_2-vortex transition has been studied mainly on the triangular-lattice Heisenberg antiferromagnet. Indeed, recent Monte Carlo (MC) simulation upto $L = 1536$ suggested the occurrence of Z_2-vortex transition at a finite temperature [2]. However, 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 [2]. In order to clarify the existence of the Z_2-vortex transition, we need larger systems beyond the spin-correlation length.

In order to perform such larger scale MC simulations, we consider an effective model of two-dimensional frustrated Heisenberg magnets. The Hamiltonian of the model is give by

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

where R_i is a $SO(3)$ rotation matrix on the site i, and $\sum_{\langle i,j\rangle}$ means the sum over the nearest-neighbor pairs on the square lattice. We have implemented MPI parallelized Wolff-Swendsen-Wang type cluster algorithm and investigated nature of possible Z_2-vortex transition by extensive MC simulation. In this CMSI project, we performed MC simulation for $L \leq 4096$. We also performed calculations for $L = 8192$ by using another resource.

In order to check the equilibration of the MC simulations, we prepare two types of initial condition: one is the ground state of the model and the other is a random state. By comparing two types of data sets starting from different initial conditions, we confirmed that our MC steps are enough long to remove the effect of initial conditions.

A preliminary extrapolation of the characteristic temperature extracted from the order parameter of the Z_2-vortex transition leads $T_v/J \simeq 0.275$. At this temperature, the spin correlation length is estimated about from 5000 to 10000 lattice spacings. Because the present system is limited $L \leq 8192$ comparable to the correlation length, we need a careful analysis to conclude the existence of the finite-temperature topological phase transition.

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Photo-induced electron dynamics in nanostructures and development of quantum devices with optical and electronic functionality

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A light and matter (LM) interaction in molecules is a fundamental physical phenomenon for understanding their physicochemical properties. We usually assume two conditions in the conventional theoretical approach to optical response of molecules: (i) Wavelength of incident light is considered to be much longer than molecular size, i.e., dipole approximation. Thus, a target molecule is well approximated by a point dipole and the dipole feels an external uniform electromagnetic field. (ii) Electric polarization in a molecule induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an “optical near filed”, according to Maxwell’s equations. However, such a self-consistent light-matter interaction between electron and electromagnetic field dynamics is ignored.

The optical near-filed confined in a nanometer-sized region induces characteristic physical and chemical phenomena. To understand such LM interaction in a nanoscale region, we must develop a more general optical response theory, i.e., nano-optical response theory taking account of nonuniform and self-consistent LM interactions and a corresponding computational code suitable for large nanostructure systems of more than ten-nanometers in size.

In our group, we have developed a generalized theoretical description beyond the conventional optical response theory invoking the dipole approximation. In our theoretical approach, electron dynamics in a nanostructure interacting with an electromagnetic field is described by the time-dependent Kohn-Sham (TDKS) equation based on minimal coupling Hamiltonian with Coulomb gauge. Electromagnetic field dynamics, on the other hand, is represented by the microscopic Maxwell's equations. The nonuniform LM interaction is taken into account in the vector potential and the self-consistent LM interaction is described by solving the electron and electromagnetic field coupled equations self-consistently. The coupled equations are solved numerically by using our developed computational program [1] (GCEED: Grid-based Coupled Electron and Electromagnetic field Dynamics). Our computational approach is based on a finite-difference method in real-time and real-space. Since the approach employs very simple algorithms, it is very suitable for massively parallelized computations. We have carried out the GCEED program by utilizing the System C, FUJITSU PREMEHPC FX10, in the Supercomputer Center at the Institute for Solid State Physics. Our theory and its computational applications to nanostructures clearly illustrated that the optical-near-field interaction induced unusual phenomena that are completely absent in the conventional optical response under the dipole approximation.

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Development of multicomponent quantum chemistry based on stochastic method for material design

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In our project we would like to focus on the hydrogen-bonded systems with multi-component quantum chemistry for material design. It is important to take account of the nuclear quantum effect and thermal effect. For example, in the case of $H_3O_2^-$, the experimental hydrogen-bonded structure where the proton is located at the center between two oxygen atoms is reproduced by the calculations including nuclear quantum effect [1, 2].

In this year, we have widely explored nuclear quantum effect and thermal effect on deprotonated hydrogen sulfide dimer anion $H_3S_2^-$, composed of second row elements, by *ab initio* path integral molecular dynamics (PIMD) simulation. At low temperature, the hydrogen-bonded proton tends to be diffusively located at the center between two sulfur atoms, which is the character of the low-barrier hydrogen bond (LBHB). This is the first case of the LBHB composed of the second row elements, although the hydrogen-bonded distance in $H_3S_2^-$ (over 3.4 Å) is much longer than the previously reported LBHB composed of first row elements (less than 2.5 Å). At high temperature, the distance between two sulfur atoms is longer than that at low temperature, and the hydrogen-bonded proton localizes to each sulfur atom. Similar tendency is obtained in the deuterated $D_3S_2^-$ species at all temperature.

Analyzing the relationship between the position of the hydrogen-bonded proton and the quantum fluctuation effect of the proton, we elucidate that the LBHB is induced by the quantum tunneling at low temperature, while such trend becomes weak and the character of LBHB vanishes at room temperature for $H_3S_2^-$.

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