3.5 SCCMS projects

First-Principles Electronic-Structure Calculations and Device/Process Simulations

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Figure 1: EM transformation of the RSDFT Hamiltonian. The left panel shows mesh points (small gray dots) in three unit cells of a [100] Si nanowire with diameter of 1 nm. The rectangular $N_{\text{RSDFT}} \times N_{\text{EM}}$ real-valued basis matrix Φ is constructed in order to obtain a computationally inexpensive N_{EM} -dimensional model of a quantum chain with Hamiltonian h_{EM} which reproduces the scattering states Ψ_{RSDFT} within the transport energy interval.

With continuing advances in semiconductor fabrication technology, it is predicted that the physical channel length in electronic devices will scales down to sub-10 nm regime. Semiconductor nanowires (NWs) have been recently considered as promising novel devices to realize the scaling merit in the ultra-small scale. However, it is also anticipated that their practical implementation will face technical issues such as characteristics fluctuations. Theoretical study of the device performance of NW transistors requires detailed atomistic transport simulations based of first-principles modeling of semiconductor nanostructures.

We here report on our recent progress in developing a first-principle quantum transport simulator based on the real-space density functional theory (RSDFT) [1] and the Troullier-Martins pseudopotentials [2]. The RSDFT method has been shown to be applicable to large atomic clusters and nanowire structures which enables one to obtain an optimized nanostructure geometry and the Kohn-Sham Hamiltonian in the real-space representation. In this work, we utilize the R-matrix method [3] and perform RSDFT-based non-equilibrium Green 's function (NEGF) transport simulations in a ballistic regime

In scope of the R-matrix method, the computational domain is split into a set of fragments (i.e. small clusters of mesh points) and the Rmatrix propagation algorithm is used for constructing the Green's function in the close device with no leads attached. The contact self-energies are computed independently at the end of calculation. This would generally involve a difficult numerical task of computing all the outgoing/decaying Bloch states in the leads. However, since the current is actually formed by mobile carriers in a few scattering states, one can make use of an appropriate low-dimension equivalent transport model (EM) to obtain the relevant physical solutions within a transport energy interval (Fig. 1). Small size of the EM representation greatly simplifies atomistic transport simulations [4].

We have developed a parallel computer code for

constructing the EM representation within an arbitrary finite energy interval. The primary lowdimensional atomistic basis is extracted from a set of Bloch states computed at equidistant set of kpoints in the Brillouin zone by the FEAST method [5]. Extra basis states are further constructed by minimizing the number of branches in the electronic band structure. Effective algorithms have been developed for optimizing parameters in the variational functional [4] and choice of the initial variational state. The numerical tests in a thin SiNW with diameter of 1 nm have confirmed applicability of the method within a wide energy range in both conduction and valence bands. For an ideal nanostructure, the EM provides an effective quantum chain model with equivalent transport characteristics. In general case, one can still make use of the EM in the lead area in order to compute the equilibrium states in the leads and obtain the contact self-energies in the NEGF formalism. The numerical tests confirm that such mixed EM-RSDFT representation causes no unphysical reflection at the contact interfaces and describes correctly the electron transport through the device channel.

Figure 2 presents an example of calculated IV characteristics in a [100] NW MOSFET with 10 nm gate length and 1 nm channel diameter. In these simulations, we have assumed a continuous dielectric layer in the insulator region and used the bulk parameters to account for polarization effects in the device electrostatics. More accurate analysis would require self-consistent calculation of the polarization charge distribution in the nanostructure which can also be greatly accelerated by implementing the EM representation.

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Figure 2: Current-voltage characteristics and potential profiles in a n-SiNW MOSFET. The first-principle RSDFT method is only used in the silicon core region. The oxide layer in the gate region is treated as a continuous dielectric media, and the device electrostatics is calculated using the bulk parameters $\epsilon_{\rm Si} = 11.9$ and $\epsilon_{\rm SiO_2} = 3.8$.

Nano-Optical Response Theory and Computational Design of Photo-Electronic Functional Devices

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Optical response of materials provides the basis for understanding their essential physicochemical properties and these optical properties are the key ingredient in developing new optoelectronic or photo-electronic devices. In conventional theoretical approaches to optical response of materials, two conditions are usually assumed:

(i) A scale of wavelength of an incident light is considered to be much longer than the material size, *i.e.*, dipole approximation. Then, a target material is well approximated by a point dipole and the dipole feels a spatially uniform electromagnetic field.

(ii) Electric polarization in material induced by incident light excitation inevitably generates a new electromagnetic field, referred to as an "optical near-filed (ONF)." However, such a self-consistent light-matter (LM) interaction between electron and electromagnetic field dynamics is ignored.

Recent development of nanofabrication and nano-optical techniques requires a more general optical response theory fully taking account of *nonuniform and self-consistent* LM interactions.

We have so far been developing a nano-

optical response theory and a computational program to describe full (nonuniform and selfconsistent) LM interactions with the aim of understanding the ONF excitation dynamics in nanostructures of more than ten-nanometers in size. Electron dynamics in nanostructures interacting with an electromagnetic field is described by the time-dependent Kohn-Sham equation. whereas electromagnetic field dynamics 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 selfconsistently. The coupled equations are solved numerically using developed by our computational program (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 highly suitable for massively parallelized computations. By using GCEED, we elucidated unique optical response phenomena due to the ONF excitation

dynamics. More specifically, second harmonic excitation of a para-dinitrobenzene molecule [1] and direct wave vector excitation of a silicon semiconductor have been investigated. These theoretical findings are expected to design photo-electronic functional devices.

We also launched a project of computational design of heterogeneous catalysts to develop efficient and commercially appealing ones, thus reducing the use of expensive rare catalytic metals [2-4]. The calculations were carried out by using the first-principles Car-Parrinello molecular dynamics approach. The theoretical approach allows us to treat dynamical chemical reaction processes taking account of the effects of temperature and nonequilibrium interactions on a heterogeneous surface or an interface.

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Superconducting correlations of nonequilibrium states

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Realizing superconductivity at room temperature is one of dreams in condensed the physics. Although matter highest superconducting critical temperature T_c at ambient pressure has been recorded in copper oxide superconductors around 130 K decades ago, it has essentially remained unchanged [1]. One reason would be that the strong effective attraction between electronic carriers required for higher $T_{\rm c}$ unavoidably drives the tendency for charge inhomogeneities. In order to circumvent this difficulty, we need to pursue a new way for controlling and enhancing superconductivity.

Recently, superconducting properties such as gap formations above room temperatures were reported in pump-probe laser measurements with the intension to excite coherent phonons in cuprates [2, 3]. These studies have shed new light on the realization of room-temperature superconductivity by utilizing nonequilibrium conditions.

In this project, we have proposed an alternative possibility ascribed to a mechanism more generic to strongly correlated electron systems. Our strategy is to control electron correlations by using the dynamical localization effect [4], where the electron hopping is effectively suppressed by the intense alternating-current electric field at high frequency. We are also inspired by recent finding that the effective attraction between carriers increases from intermediate to strong coupling regions in strongly correlated electron systems [5].

To achieve our goal, we have performed the many-variable variational Monte Carlo (mVMC) [6, 7] calculations for the Hubbard model on square lattice under laser irradiation introduced by means of the Peierls substitution. The mVMC method is capable of providing us flexible and accurate quantum states in correlated electron systems for not only equilibrium but also nonequlibrium at zero temperature.

As a result, we have found that the superconductivity can be enhanced by strong laser irradiation. We have shown that this enhancement is caused by an intrinsic effect of the dynamical localization. More importantly, this enhancement is numerically achieved without causing substantial charge inhomogeneities in contrast to the equilibrium ground state. We have also found that the dynamical superconductivity is subject to the Higgs oscillations during and after the irradiation. Our findings have revealed a way to enhance superconductivity that is inaccessible in equilibrium in strongly correlated electron systems.

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First-Principles Phase Field Mapping I

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To perform, for example, accurate mapping of first-principles results to phase field models, it would be necessary to perform a lot of firstprinciples calculations to collect important information on (1) the behavior of variety of chemical reactions and (2) the relationship between the geometrical and electronic structures of various materials. For the purpose of (1), we performed first-principles molecular dynamics simulations of the chemical reactions of carbon monoxide (CO) and hydrogen atoms to produce methanol by using time-dependent density functional theory (TDDFT) and timedependent GW (TDGW) method in particular for the electronic excited state for the first time [1]. For the purpose of (2), we also performed various (ferromagnetic and anti-ferromagnetic) crystalline phases of MnO₂ [2] and various cap structures shown in Fig. 1, with which one side of the armchair carbon nanotubes are terminated [3], and clarified the relationship between their geometrical and electronic structures. Last, We investigated a mechanism of generating a screw dislocation of graphite and proposed a way to create a carbon nanocoil inside an insulating SiO₂ cylinder with a bottom surface and a pillar at the center [4].



Fig.1 Various cap structures of armchair carbon nanotubes investigated in Ref. [3].

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First-Principles Phase Field Mapping II

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To perform, for example, accurate mapping of first-principles results to phase field models, it would be necessary to perform accurate and reliable first-principles calculations. For this purpose, we performed self-consistent GW total energy calculation of He dimer with different interatomic distances using TOMBO [1] and derived the adiabatic potential between He Then, using it, we solved atoms. the Schrödinger equation for the two He system and estimated the van der Waals interaction between two He atoms. Surprisingly, the resulting expectation value for the interatomic distance of He dimer is quite large (~ 35 Å) [2]. In order to obtain accurate photoelectron (PE) and photoabsorption spectra, we performed for the first time [3] the self-consistent GWF calculation for small molecules using TOMBO. The accuracy of the result is comparable or higher than the result of the multi-reference single & double configuration interaction method as shown in Tables I and II. Last, we proved that the PE spectroscopy and therefore the quasiparticle (QP) theory can be applied to an arbitrary initial excited eigenstate [4]. The validity of the present theory for some initial excited eigenstates is tested using the one-shot GW approximation using TOMBO for several atoms and molecules [4].

TABLE I. Ionization potential (IP), electron affinity (EA), and optical gap E_g^{opt} (corresponding to ${}^2S \rightarrow {}^2P$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions) of Na and Na₃ (in units of eV).

	Na			Na ₃		
	IP	EA	E_g^{opt}	IP	EA	E_s^{opt}
G_0W_0	5.15	0.41	1.32	4.10	1.14	0.53
GW	5.40	0.33	2.23	4.64	0.51	1.91
LGW	5.23	0.42	2.18	4.48	0.66	1.92
LGWT ₂	5.01	0.60	2.00	4.08	1.04	1.57
LGWTw	5.12	0.58	2.16	4.04	1.15	1.60
MRDCI	4.97^{1}	0.44 ^b	1.98 ^b	3.76 ^c	1.07/1.17 ^b	1.61 ^b
Expt.	5.14 ^d	0.55°	2.10 ^f	3.97 ^s	1.02/1.16 ^h	1.65 ⁱ

TABLE II. IP, EA, and $E_{g^{\text{opt}}}^{opt}$ (corresponding to the ${}^{3}\Sigma_{g}^{-} \rightarrow {}^{3}\Sigma_{u}^{-}$ transition) of B₂, and IP and $E_{g^{\text{opt}}}^{opt}$ (corresponding to the ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{1}\Pi_{u}$ transition) of C₂H₂ (in units of eV).

		B ₂			C_2H_2	
	IP	EA	E_g^{opt}	IP	E_g^{opt}	
G_0W_0	9.21	2.18	2.44	11.05	5.01	
GW	9.97	1.76	3.94	11.65	8.39	
LGW	9.79	1.94	3.75	11.44	8.23	
$LGWT_W$	9.87	1.91	3.84	11.48	8.25	
MRDCI	9.48 ^a	2.0 ^b	3.85°	11.21^{d}	(8.06) ^e	
Expt.	10.3 ± 0.6^{f}	$1.8{\pm}0.4^{g}$	3.79 ^h	11.49 ⁱ	8.16 ^j	

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Energy conversion and storage – electric energy Osamu Sugino

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We have studied the structure and catalytic property of a zirconia (ZrO₂) surface, which has been developed as the post platinum cathode material of a future fuel cell. Zirconia is attracted attention because it is very stable but can efficiently catalyze the oxygen reduction reaction (ORR) when partially reduced and doped with nitrogen atoms. To explain how and why ORR occurs, we did a first-principles calculation of the electronic structure using the VASP package implemented in the ISSP supercomputer.

The surface was modeled using ZrO₂(101), which is the most stable among the tetragonal surfaces. The 2x2 ZrO₂(101) was prepared as shown in Fig. 1 and let water molecules adsorb to represent the complex hydrated surface. The slab model was then doped with up to two nitrogen atoms and removed by up to one oxygen atom to mimic the doped and reduced interface. The surface was then covered with ORR intermediates such as O and OH under all possible coverage conditions to investigate the ORR pathways.

The calculated adsorption energy of an oxygen atom is negative indicating that it is not adsorbed on the surface and therefore is nonreactive when undoped. When doped, the



Fig. 1: ZrO2(101) model.

adsorption energy is 0.22 eV for a certain configuration of the impurities, indicating that the surface can be made reactive by doping.

The obtained free-energy profile of ORR shows that the activation barrier of the whole reaction is half an eV because of too weak binding of an oxygen molecule, indicating that the surface is not so reactive even after doping and thus does not model the real catalyst.

Nevertheless, our calculation shows that ORR occurs without being hampered by the two-electron reduction process to produce a hydrogen peroxide in consistent with experiments. Since the two-electron reduction usually occurs on an electrocatalyst of weak oxygen adsorption, such as gold, the zirconia surface is exceptional. We find that this behavior is due to the complex hydrated surface structure; the two-electron reduction is hindered by the OH adsorbed near the reaction site. Note that the complex hydrated structure requires us to use a quite large unit cell for the calculation, which is infeasible with smaller computers.

Slow Dynamics in Ionic Liquids

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Ionic liquids (ILs), recently, are attracting tremendous interests both in application and fundamental research, due to their outstanding thermo-physical and chemical aspects. One of the features is the low glass-transition temperature, that can be below the room temperature. Ability of high supercooling endorses ILs promising as electrolytes, solvent for many organic and inorganic liquids. Our focus, here, is to understand the slow dynamics in ILs, especially on the aspect of alkyl-chain length and electrostatic interaction.

The systems we investigate is imidazoliumbased ILs, 1-Alkyl-3-methylimidazolium phosphate and borate [1], which is a prototype of hydrophobic and hydrophilic system respectively. For the imidazolium family, a distinguishing pre-peak is found in the static structure factors, indicating a still unclear mesoscopic ordered structure in liquid state (at a length scale about 10 nanometers) [2]. This demands large length scale simulation. On the ISSP clusters, three different system sizes will be investigated, i.e., 1000, 8000, and 27000 ion pairs, which is roughly corresponding to 27000, 216000, and 729000 atoms in the simulation box. As the dynamics of the system is very slow at the temperature near roomtemperature, long-time structural relaxation is needed, which will be about 10-100 nanoseconds.

In order to elucidate the role played by the non-charged alkyl-chain and the charges on the head of cations and anions for the dynamics of the system, two series of systems has been numerically investigated. One is systematic change of the chain-length, varying from 2 to 16 carbons on the alkyl chain. The other approach is charge-scaling, where the charges on the ions will be scaled in the range 0.6 to 1 proton. Detailed analysis on the effect of molecular geometry and electrostatics is ongoing, on which we plan forthcoming publications in a near future.

Let us mention brifly our plan. For analysis of the dynamics, usual two- (and four-) point correlation function will be calculated. These correlators would show systematic change as the chain-length and scaled charges. The vibrational density of states is another candidate to be analyzed, in terms of how the extra vibrational modes (e.g. optic modes) affect the relaxation behavior of the system, which is absent in usual glassy systems (e.g. metallic melts, colloids, polymers, and granular materials).

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Promotion of joint researches through Project for advancement of software usability in materials science in 2015

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1 Introduction

In fiscal year 2015, the numerical solver package for quantum lattice model $\mathcal{H}\Phi[1]$ was developed by "Project for advancement of software usability in materials science" by The Institute for Solid State Physics, The University of Tokyo[2]. By using $\mathcal{H}\Phi$, we can calculate physical quantities in quantum lattice models that are constructed by one- and two-body interactions by using exact diagonalization with Lanczos method and thermal pure quantum states[3]. In fiscal year 2016, we investigated the origin of charge glassy state observed in organic conductors on the basis of the spinless fermion model and also constructed the solver to analyze spin relaxation phenomena in quantum dots.

2 Spinless fermion model

Quasi two dimensional organic conductor theta-type BEDT-TTF salts are considered as typical geometrically charge frustrated system and theoretically studied within the effective quantum models such as extended Hubbard model and spinless Fermion model[4]. Recently, in terms of charge ordering transition and glassy behavior, the importance of long range Coulomb interaction (LRC) is indicated[5].

In this study, we extended $\mathcal{H}\Phi$ to treat the spinless fermion model up to 6×6 sites. Then, we investigated the properties of the ground state by exact diagonalization method on the spinless fermion model with LRC in the presence of the geometrical charge frustration. Furthermore, we also calculated physical quantities at finite temperatures such as charge structure factors, specific heat and entropy by using thermal quantum pure state. From these calculations, we found that with increasing LRC, the wave number dependence of charge structure factors becomes broadened and the release in entropy by decreasing temperature becomes gradual in the intermediate temperature region. These results indicate that, compared to the short-range geometrical charge frustrations, LRC enhances the competition among various types of charge order patterns and thus promotes the metastable states in the intermediate temperature region.

3 General electron model

In experiments of GaAs/AlGaAs quantum dot systems, the spin relaxation rate of the highspin state is more than 10 times larger than that of the S = 0 state. However, this large relaxation rate can not be simply explained by the electron number dependence and the angular momentum selection rule. In this project, we extend the function of $\mathcal{H}\Phi$ to investigate the many-body effect in the high-spin states of quantum dots, and examine how the electron correlation and the spin-orbital interaction influences spin relaxation. Since the number of the two-body interactions becomes enormous in this model, we have first implemented the parallelization on the interaction parts and succeeded in improving the efficiency of calculation. As a result, the calculation of the eigenstates in 32-site systems was achieved within the configuration interaction method on the basis of Fock-Darwin single-particle states. We are now estimating the spin relaxation rate, and will compare experimental results on spin relaxation in the high-spin states of quantum dots in the near future.

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Many-variable variational Monte Carlo study for interfaces of high- T_c superconductors

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Recent experiments on interfaces and thin films of the cuprates and iron-based superconductors suggest that they often show better superconducting properties such as higher critical temperatures (T_c) than in the bulk materials. Above all, in a recent experiment on the interfaces of $La_2CuO_4/La_{2-x}Sr_xCuO_4$ (interfaces of the Mott insulator and the metallic phases), unexpected pinning of the T_c has been found [1] by systematically changing the doping rates of the metallic phase. It is noteworthy that pinning $T_c \sim 42$ K is nearly the same as the optimal T_c in the bulk $La_{2-x}Sr_xCuO_4$. This behavior is in a sharp contrast with the bulk system where a dome-like doping dependence of T_c has been commonly found in the doping concentration dependence.

To clarify microscopic origin of the unconventional pinning of T_c observed at the interfaces of La₂CuO₄/La_{2-x}Sr_xCuO₄, we study multi-layer Hubbard model as an effective model for interfaces of the cuprates by using many-variable variational Monte Carlo method, which properly takes into account both spatial and dynamical quantum fluctuations [2, 3, 4, 5]. We employ the parameter values within the realistic constraint of the cuprate interface suggested from the experimental results and ab initio calculations. Especially, we take into account the effects of inter-layer Sr diffusions as differences in on-site levels around the interfaces.

As a result, we find that pinning of carrier densities and superconducting correlations at the interfaces indeed occur in the multilayer Hubbard model [6] in essential agreement with the experimental results. We also clarify that the pinning emerges as a consequence of the inter-layer phase separation, which dissolves the inner-layer phase separation. Our result shows that the interfaces provide an ideal tool to enhance and stabilize superconductivity without fine tuning and opens a new way to design the higher- T_c superconductivities.

A part of calculation is done by using opensource software mVMC [3].

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First-principles analyses on adsorption of NH_x on GaN surfaces

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Gallium nitride (GaN), which belongs to the III-V family, is attracting tremendous attention recently. Owing to having wide bandgap, GaNis used in optoelectronics, photonics, high power and high temperature operation devices. Having well knowledge about thesurface adsorption and deposition mechanisms for different precursors isnecessary to improve thin-film crystalline quality and growth processrequirements. Using density functional theory (DFT) method, as implemented in realspace density functional theory (RSDFT) [1], we aim to theoretically investigate the reaction mechanism of GaN on (0001) surface from ammonia (NH₃) precursor. The calculated lattice parameters (a = 3.2 Å, c = 5.2 Å) are in accordance with experiments [2]. The 2x2 surface reconstruction structure is obtained. We found that, in agreement with other study [3], Ga add atom is most favorable to form at hcp



Figure 1: (left) Ga-hcp and (righ) N-fcc add atom configurations. All lengths are in Å.

Table 1: Bin	nding enei	gies of	NH _x (x=	=1,2, and	3) on	clean
(upper) and (Ga adatom	(bottom) surface	ès.		

	On top	Нср	Fcc	Bridge
NH ₃	-0.0479 -0.0465			
NH ₂	-0.1725 -0.1456	-		-0.1768 -0.1196
NH	-0.2317	-0.2449	-0.2715	

site, while N add atom is most favorable to form at fcc site. The obtained structures for Ga and N add atom surfaces are shown in Figure 1.

Next, adsorptions of NH₃, NH₂, and NH on bare and Ga adatom surfaces were studied. We found that on the bare surface, NH₃ is the most favorable to form at on top site, NH₂ is likely to form at the bridge site, and NH is the most stable at the fcc site, respectively. On the Ga adatom surface, all NH₃, NH₂, and NH are the most favorable to form at on top site. The calculated binding energy for NH₃, NH₂, and NH on the bare and Ga adatom surfaces at on the top, hcp, fcc, and br sites are summarized in Table 1. This surface specificity of binding energies suggests that there exist different kinetics during the growth of GaN on surface.

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First-principles calculation of interactions between extreme pulse light and matter

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Interaction between intense and ultrashort laser pulse and solid is one of active subjects in current optical sciences. Employing a few-cycle femtosecond laser pulses, a number of intriguing phenomena reflecting extremely nonlinear light-matter interactions have been observed. We have been developing a firstprinciples computational method to describe electron dynamics in solids under irradiation of a pulsed electric field based on time-dependent density functional theory, solving timedependent Kohn-Sham equation in real time for electron orbitals in a unit cell of crystalline solids.

For a quantitative description of light-matter interactions, it is important to employ a potential in the Kohn-Sham equation that describes the band gap of the material adequately. As is well known, a simple local density approximation underestimates the band gap systematically. Recently, a few potentials that describe band gaps reasonably have been proposed. We have investigated computational methods to use such potentials in our code and examined optical responses of dielectrics in both linear and nonlinear regimes [1].

We implemented two potentials in our code, a meta-GGA potential developed by Tran and Blaha and a hybrid functional of Heyd, Scuseria, and Ernzerhof. For the meta-GGA potential, we have found that a predictorcorrector step is essential for a stable time evolution. Since a computation of nonlocal exchange potential in the hybrid functional requires heavy computational costs, we have developed a code that efficiently utilizes GPU.

We applied the code to various optical phenomena. One of such applications is the nonlinear photogalvanic effect [2]. It was found that an extremely intense and ultrashort laser pulse produces a current in dielectrics of wide band gap. We have found that the induced current in such dielectrics shows complex behavior, changing its direction depending on the maximum intensity of the pulse.

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Tensor-Network Computation of Generalized Kitaev-Heisenberg Model*

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Realization of Kitaev spin liquid is an active research topic of recent years since Jackeli and Khaliullin pointed out that Iridium compounds mav be promising candidates. Among them, an effective quantum spin model for Na2IrO3 was derived [1] from the firstprinciples calculation, which then studied by exact numerical was diagonalization (ED) of a 24 site cluster. The resulting model contains that а parameter, Δ. controls the proximity to the pure Kitaev model (Δ =0 for the pure Kitaev model. Δ =-28 meV for the first-principle model). According to diagonalization the exact calculation, there are 4 phases; 3 distinct incommensurate magnetically ordered phases and a commensurate ordered phase. so-called zigzag-Z phase.

In our project using the ISSP supercomputer. carried we out tensor-network calculation of the same model, to verify the validity of the small-cluster ED results. In the tensor network calculation, one assumes that the wave function is represented by а partially contracted external product of many tensors, whose elements are obtained by some iterative optimization or variational adjustments. To be more specific, our calculation is based on the iPEPS ansatz that is expected to reproduce the thermodynamic limit results accurately as far as the entanglement is small and the magnetic structure fit in the We employed assumed unit cell. the update'' ``simple technique for optimizing the tensor elements. The accuracy of the method is controlled by the bond dimension, i.e., the dimension of the indices to be The contracted. largest bond dimension we used in the calculation was 9.

While our new results identifies the character of the first-principle model to be the zigzag-Z phase, in agreement with the small cluster ED result, they also revealed that the Δ -phase diagram is significantly different from what had been predicted the ED For by result. one of example. the incommensurate phase turned be out to а commensurate phase with a unit cell of 16 sites.

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Simulation of organic-inorganic interfaces

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In the fiscal year of 2016, we have mainly treated two subjects using our hybrid quantum-classical (QM-CL) simulation codes.

Subject 1: The hybrid QM-CL simulation of Si-O bond breaking in silica glass [1]. We perform a hybrid QM-CL simulation of a 4,608-atom silica glass at a temperature of 400 K with either a water monomer or dimer inserted in a void. The quantum region that includes the water and the surrounding atoms is treated by the DFT. During a simulation, the silica glass is gradually compressed or expanded. No Si-O bond breaking occurs with a water monomer until the silica glass collapses.

With a water dimer, we find that Si-O bond breaking occurs through three steps in 3 out of 24 compression cases: (i) H-transfer as $2H_2O \rightarrow OH^- + H_3O^+$ accompanied by the adsorption of OH⁻ at a strained Si to make it five-coordinated, (ii) breaking of a Si-O bond that originates from the five-coordinated Si, and (iii) H-transfer from H_30^+ to the O of the broken Si-O bond. A separate DFT calculation confirms that the barrier energy of the bond breaking with a water dimer under compression is smaller than that with a water monomer and that the barrier energy decreases significantly when the silica glass is compressed further.

Subject 2: Moisture-Induced Reduction of Adhesion Strength Between Surface Oxidized Al and Epoxy Resin: Dynamics Simulation with Electronic Structure Calculations [2]. Adhesion strength between metal and epoxy resin is well known to reduce significantly in a moist environment. To theoretically understand its mechanisms, we calculate the shear strength of the interfacial adhesion between the surface oxidized Al and bisphenol-A epoxy resin with a varying number of water molecules or hydroxide ions inserted inbetween using the hybrid quantumclassical simulation method. The quantum region in the hybrid method, which is composed of about thousand atoms at the interface, is treated by the electronic densityfunctional theory implemented to calculate on a real-space grid. In a typical run using 63 CPU's, it takes about 9 minutes to evolve the atomic dynamics by a timestep; here, the settings of the parallel computation are the spatial decomposition of 5x5x5, the electronic level parallelization of 2, and the OpenMP parallelization of 4.

It is thereby found that the adhesion strength reduces more significantly as the degree of the moisture content increases, in accordance with experimental the observations. Microscopic analyses find the following key features; (i) The inter-atomic Al-O bond between the Al atom of the oxide and the O atom of the epoxide group in the epoxy resin contributes substantially to the strength of the interfacial adhesion. (ii) Dissociation of the O atom of the epoxide group forming such an Al-O bond is enhanced when an H₂O rather than an OH resides in close proximately to the bond. (iii) The epoxy resin becomes more plastic by incorporating H₂O molecules. Both (ii) and (iii) act to weaken the shear strength of the interfacial adhesion.

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

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Organic photovoltaic (OPV) cells and Perovskite solar cells are being eagerly researched and developed. In particular, bulk heterojunction (BHJ) type of the organic photovoltaic cells has many attractive properties. Although exciton dissociation that leads to generation of free carriers has been considered as a key factor in photoconversion process of OPVs, the fine mechanism of the exciton dissociation against Coulomb interaction has not been fully revealed yet.

Then, we studied three properties; (1) The first one is a "descriptor" of efficiencies of free carrier generation [1, 2]; (2) band bending by deformed structure of organic compound at the interface in the BHJ [3]; and (3) blending effects of electrondonor and -acceptor materials in the BHJ [4]. In these studies, we used our original code named as MolDS [5] implemented for massive parallel computing of semiempirical quantum calculations, especially electronic excites states in large molecular aggregates, by using hybrid (openMP/MPI) parallelization technique.

In the first part, we found that a pair of donor and acceptor exhibits the largest charge-bridging upon photoabsorption, which leads to the highest IQE and PCE. In the second part, we revealed two different dynamics of free carrier generation, prompt (a few picoseconds) generation from excitons that were generated on interfaces and delayed (order of sub-nanoseconds) generation from excitons which migrated to interfaces; the former is dominant but its ratio depends on the domain size of morphologies. Finally, the band bending in OPV due to the structure fluctuations are revealed quantitatively as 0.0, 0.2 or 1.5 eV at the edge-on interface between PCBM and rr-P3HT, rra-P3HT or F-P3HT.

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Conversion and storage of energy-fuel cells and secondary batteries: Research and development of fundamental technologies of battery simulators.

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The goal of our project is to develop the basic technology of the whole battery simulator. One of the key techniques is molecularlevel design of polymer membranes controlling transportation of protons and ions across the membrane with proper stiffness resistant to mechanical deformation under external stress. Such membranes are expected to be widely applicable to the fuel cells used in the industrial products.

On the system B and C, we performed fully atomistic molecular dynamics (MD) calculations of hydrated perfluorosulfonic acid (PFSA) ionomers composed of a hydrophobic polytetrafluoroethylene backbone with hydrophilic side chains terminated by sulfonic acid (its molecular structure is shown in Fig. 1), as a model of proton exchange polymer electrolyte membrane of fuel cells^[1]. The morphology of the hydrated polyelectrolyte membranes, depending on the degree of hydration and lengths of backbone monomer and side chains, was investigated. Diffusivity of water molecules in the PFSA membranes, which is closely related to the proton transport in the membranes, was also measured as a function of the degree of hydration. Further, mechanical resistance to the tensile deformation of the polymer membranes was tested.

We found that an increase of hydration changes the morphology of the hydrated PFSA membranes from a channel-network structure to a tortuous layered structure shown in Fig.



Figure 1: Molecular structure of perfluorosulfonic acid (PFSA) ionomers.



Figure 2: Number density map of sulfonic acid groups, water, and hydronium ions at one cut plane. λ is a mole fraction of water molecule and hydronium ion to sulfonic acid groups.

2, and that water diffusivity and mechanical resistance to the stress strongly depend on the degree of hydration. These findings will contribute to the development of higher performance fuel-cells and secondary batteries and to the realization of the entire battery simulator in the near future.

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Multiscale simulations of bio-membrane shape-changing dynamics

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In the cell, various shape-changing processes of membrane happen. For example, in the process called endocytosis/exocytosis, a vesicle fusion/fission happens with a help of protein machinery. We are interested in these membrane shape transformations driven by proteins.

Molecular simulations of the membrane shape transformation are challenging due to size of the system. All-atom molecular dynamics simulations are quite expensive since total number of atoms can easily exceed one million. Alternatively, we can use coarsegrained models to reduce the computational cost.

In this study, we use a coarse-grained model in which a lipid molecule is represented by three beads, developed by Noguchi and coworkers [1]. The model has been confirmed to reproduce some basic properties of lipid membrane, including spontaneous vesicle formation. As a test calculation, I simulated vesicle formation from flat membrane. Order parameters defined using principal axis clearly quantify the shape transformation. By using this coarse-grained model, I am trying to reveal how proteins induce the shape transformations. Especially, banana-shaped proteins in the BAR domain family play an important role by generating curvature on the membrane. I am particularly interested in one of the BAR domain proteins called Pacsin [2] that transforms homogeneous vesicles into various shapes.

To simulate this protein-induced shape transformation, I am implementing a coarsegrained protein model in the afore mentioned model. I am considering internal energy such as bond length, bond angle and contact potentials as well as inter-molecule energy such as electrostatic interaction between lipid head groups and charged residues in the protein.

This work is in collaboration with H. Noguchi (ISSP, The University of Tokyo).

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Excited-state calculations for molecular aggregates based on Green's function method

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Predicting the electronic excited states of large systems with reasonable accuracy remains an ongoing challenge in quantum chemistry. In this project, we aim to develop a theory that can treat excited states of large systems with reasonable accuracy, on the basis of the fragment-based electronic structure theory and many-body Green's function techniques. As a first step, we have developed a theory to treat non-local excitations in large systems based on the configuration interaction singles (CIS) and fragment molecular orbital (FMO) method. The developed method was applied to organic donor/accepter interfaces.

The present theory is the generalization of the excite-state calculations combining the FMO and transition-density fragment interaction methods [1]; the theory was designed to reproduce low-energy excited state manifold of large systems with small dimension. The aim of the development is to systematically derive a tight-binding exciton Hamiltonian, which can be used to study real-time quantum dynamics combined with quantum dynamics theory. To describe delocalized excited state for the total system, configuration state functions (CSFs) were constructed from localized molecular orbitals by self-consistent field calculations for fragment monomer and dimer, and multi-layer FMO with the CIS method. The excited-state wavefunction of the total system was described as a superposition of fragment CSFs for local excitations and for interfragment chargetransfer excitations. Exploiting those fragment CSFs allows for the efficient truncation of the dimension of excited-state Hamiltonian. The one-electron parts of excited-state Hamiltonian were treated by the FMO-linear combination of molecular orbital (FMO-LCMO) method; the two-electron parts were efficiently treated within FMO framework. In addition, the approximation scheme to calculate twoelectron parts was developed in accordance with the electrostatic approximation in the FMO.

As a demonstration, the developed method was applied to an organic donor/accepter interface comprising 24 pentacene and 20 fullerene molecules. The excited states were treated at the FMO-CIS/6-31G** level; the FMO calculation parallelized with the flat MPI was performed in system B using 864 cores. The results were analyzed with correlation correction to the diagonal terms and the screening correction to the long-range Coulomb interactions of the off-diagonal terms. As a next step, the charge separation and recombination mechanisms will be analyzed by combining a quantum dynamics theory.

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Design of spintronics materials by order-N screened KKR Green's function method

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This year, we developed a large-scale electronic structure calculation package, KKRnano, where the full potential screened Korringa-Kohn-Rostoker (KKR) Green's function method is optimized by a massively parallel linear scaling (order-N) all electron algorithm [1]. The central part of the screened KKR Green's function method is the solution of the Dyson equation for the Green's functions $G_{LL'}^{nn'}(E)$:

$$G_{LL'}^{nn'}(E) = G_{LL'}^{r,nn'}(E) + \sum_{n''L''L'''} G_{LL''}^{r,nn''}(E)\Delta t_{L''L'''}^{n''}(E)G_{L'''L'}^{n''n'}(E).$$

Here L = (l, m), where l and m are the angular momentum indices. $G_{LL'}^{nn'}(E)$ and $G_{LL'}^{r,nn'}(E)$ are the Green's function elements of the system under study and of a suitable reference system, respectively. $\Delta t_{LL'}^n(E) = t_{LL'}^n(E) - t_{LL'}^{r,n}(E)$ is the difference between the single site scattering t matrices of the atoms in the true and reference system. In the screened KKR method, a system with strongly repulsive potentials is used as reference system [1], such that the Green's functions $G_{LL'}^{r,nn'}(E)$ decrease very rapidly at large distances $(\mathbf{R}^n - \mathbf{R}^{n'})$. Contrary to the standard KKR-GF method, KKR nano allows order-N scaling of the computational cost by truncating the Green's function and solving the Dyson equation iteratively, based on the quasi minimal residual method with block-circulant matrix preconditioning. Since the charge density and density of states are directly related to the imaginary part of the Green's function, one can use the



Figure 1: (Upper panel) Crystal structure of HEA CrFeCoNi with the random solid solution phase. (Lower panel)Local energy fluctuations of Cr atoms $(E^{\rm Cr} - \overline{E}^{\rm Cr})$ as a function of number of (a) first nearest neighbor Cr atoms $(n_{\rm Cr}^{1\rm st})$ and (b) second nearest neighbor Cr atoms $(n_{\rm Cr}^{2\rm nd})$. Green points show the average values. The inset in (b) shows the $L1_2$ crystal structure.

KKR-GF method in the framework of density functional theory.

We demonstrate large-scale all-electron density functional calculations for a prototype high entropy alloy (HEA) CrFeCoNi by the KKRnano program package [2]. HEA forms an ideal face centered cubic (FCC) or body centered cubic (BCC) random solid solution phase. To describe the randomness and local environment effect, one needs to employ a large supercell; therefore, it has been recognized that general DFT methods, where the computational costs increase as order- N^3 , cannot perform calculations. To overcome this limitation, we have executed the KKRnano program package for a supercell containing 1,343 atoms. We have also presented a new method to calculate "local energies", which is the energetic contribution of each atomic cell to the total energy of the supercell. The local energy gives the useful information for local structural stability. Our supercell calculations show very large variations of the local energies. This leads to fact that the random solid solution is not stable and has a tendency to form an L_{1_2} -structure with the Cr-atoms ordered at the corner of the cube and the elements Fe, Co and Ni randomly distributed on the three other FCC sublattices.

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Materials exploration for sodium secondary batteries

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We have studied the microscopic mechanism of charge/discharge reactions in several battery systems by means of first-principles calculations to explore new sodium secondary batteries. In this year, we focus on Na/SnS and $\text{Li}/\text{Li}_x M\text{TiO}_4$ (M=V, Mn, Fe, Co, and Ni) systems.

Tin compounds are known as high-capacity materials in charge/discharge reactions and to have advantages in price and safety for practical applications, being considered as a good candidate for the anode materials of sodium secondary battery. [1, 2] We investigate the electronic mechanism in discharge reactions of Na/SnS system. From experimental works, several stages are involved in conversion reactions starting from SnS. Stable phases in the ternary Na-Sn-S system are searched by assuming a reaction as (1-x)SnS+xNa \rightarrow Na $_x$ Sn $_y$ S $_z$ +(1-x-y)Sn + (1-x-z)S. On the basis of the total energies calculated for the reaction, Sn and Na_2S are generated as intermediate products. In addition, generated Sn and newly introduced Na may react to form several alloy phases as $NaSn_5 \rightarrow NaSn_2 \rightarrow NaSn \rightarrow Na_9Sn_4 \rightarrow Na_{15}Sn_4.$

This multi-stage discharge reaction may explain discharge voltage-capacity curve measured by Kitajou *et al.* [3] To identify possible phases in the discharge reaction, calculated x-ray absorption spectroscopy spectra for SnS and Na₂S are compared with experimental ones [3] and the existence of Na₂S in the intermediate stage is confirmed.

 $Li_x MTiO_4$ (M=V, Mn, Fe, Co, and Ni) systems have attracted much attention recently because of a possible candidate for highvoltage and high-capacity cathode materials. In this oxides, since cations M are octahedrally coordinated by O ions and octahedra MO_6 share their ridges, high stability to O dissociation is highly expected. However, measured discharge capacity is extremely lower than theoretical one and complicated processes are involved in the discharge reaction. We estimate the voltage as a function of Li concentration and O-vacancy formation energy for different M systems. From the electronic structure calculations, it is found that a two-stage process associated with M+Ti and M+O takes place depending on the Li concentration. The Ovacancy formation energy becomes decreased as the Li concentration is decreased, implying the increase of the role of O redox in the reaction. This tendency becomes more remarkable in proportional to the number of d electrons in M ions.

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Exploration of novel semiconductors by first-principles screening

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The search for novel semiconductors is increasingly important as the applications of semiconductors become more prevalent. Among the compound semiconductors, nitrides and oxides are especially attractive due to the abundant and environmentallybenign nitrogen and oxygen constituents. Currently commercialized nitride semiconductors are, however, mostly limited to GaN and its based alloys. Several kinds of oxide semiconductors are used in commercial applications such as transparent electrodes and thin-film transistors, but those with improved or different functionalities are required to expand the applications. This situation stimulates not only experimental but also computational, or in silico, exploration of novel nitride and oxide semiconductors.

Recently we have discovered a novel nitride semiconductor $CaZn_2N_2$ by first-principles screening of ~ 600 candidate materials in combination with high-pressure synthesis [1]. It is our objective to extend this *in silico* screening approach for the exploration of semiconductors with a wide variety of chemistry, not only nitrides but also others including oxides. In addition, the screening needs to be made more efficiently so that a much larger number of candidate materials can be evaluated within feasible computational time.

Our screening procedure is schematically shown in Fig. 1. In the first step, the fundamental properties, thermodynamic stability in the phase diagram, and stability against lattice vibration are evaluated for candidate materials. Selected materials are then subject to further investigation in terms of native point defect formation and doping to assess the dopability into p and/or n type. Finally, promising materials as semiconductors are proposed on the basis of these assessments.

Among the series of calculations, the native point defect and dopant calculations are computationally the most demanding and complicated. Therefore, making these calculations more efficient is an urgent requirement for accelerating the screening.

In this study, we have developed and tested computational schemes for point defect calculations. First, we tested a scheme based on non-self-consistent, dielectric-dependent hybrid functional calculations to correct the valence and conduction band edges on top of the calculations using semilocal functionals [2]. This approach allows us to obtain band edge positions with accuracy comparable to standard GW calculations at the random phase approximation level, simultaneously with much Activity Report 2016 / Supercomputer Center, Institute for Solid State Physics, The University of Tokyo



Figure 1: Schematic showing the screening procedure for semiconductors.

reduced computational costs.

Second, a finite cell-size correction scheme that we have developed previously [3], which is an extension of the method proposed by Freysoldt, Neugebauer, and Van de Walle (FNV)[4], was modified so that the corrections can be applied semi-automatically. By correcting electrostatic interactions, the formation energies of charged point defects at the dilute defect limit, in other words, infinite cellsize limit, can be predicted even using supercells with moderate sizes for diverse defects in diverse materials (Fig. 2). This is attained by the twofold extension of the original FNV scheme: (i) Anisotropic screening is taken into account using dielectric tensors and (ii) the corrections for relaxed atomic structures are significantly improved by the use of atomicsite local potential as a potential marker. This year the CPU time was mainly used for testing and establishing the above-mentioned correction schemes. As a result, these schemes are now almost ready for massive calculations toward high-throughput screening of diverse candidates.

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Figure 2: Schematic showing the finite cellsize corrections based on the FNV scheme in charged point defect calculations using a supercell approach.

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Quantum Molecular Dynamics Simulation on Electrolyte Solution for Sodium-Ion Battery

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Na-ion batteries (SIBs) receive growing attentions as the alternative to Li-ion batteries (LIBs) with shrinking resources of lithium. Electrolyte solutions, one of the main components of secondary battery, have a crucial impact on the performances of batteries. Within the electrolyte solutions, the superconcentrated solutions attract intense interests as a novel class of electrolyte for the specific favorable characteristics, i.e., high electrochemical (oxidative/reductive) stabilities, fast electrode reactions, low volatility, and so forth [1].

Career ion conductivity is one of the crucial issues in superconcentrated solutions, which generally show high viscosities. Especially, the ion diffusion mechanism is one of the remaining fundamental issues for superconcentrated electrolyte solutions, in which conventional vehicular-type diffusion mechanism cannot take place due to the severely limited number of free solvents.

The present study analyzed concentration dependences of solution structures and diffusion properties of electrolytes for SIB by using molecular dynamics (MD) simulations based on the density-functional tight-binding (DFTB) method.

DFTB-MD simulations were performed with the divide-and-conquer (DC) technique for accelerated computation by using the DC-DFTB-K program package [2] that is designed parallelized for massively computer environment such as the K computer. Modified 3ob parameter was used with so-called DFT-D3 Dimethoxy dispersion correction. ethane (DME) and Na-FSA (bis-fluorosulfonyl amide anion; $N(SO_2F)_2$) were employed as solvent respectively. and salt. Dilute and superconcentrated systems with 10% (220 molecules, 3388 atoms) and 40% (215 molecules, 2924 atoms) of salt concentrations were setup with the densities obtained from classical MD simulations. Production runs were performed for 20 ps under NVE ensemble following 10 ps of equilibration runs under NVT ensemble (T = 298.15 K).

The averaged coordination number of Na ion was ca. six for both dilute and superconcentrated systems. Oxygen atoms were dominantly contributed to the coordination. In the dilute (10%) system, the numbers of coordination of DME and FSA to Na ion were

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four and two, respectively, while that for the superconcentrated (40%) system were three for both DME and FSA (Fig. 1). The numbers of free DME (FSA) decreased from 77% (6%) to 11% (0%) with increasing concentration of salts from 10% to 40%.



Fig. 1: Coordination numbers of O, F, and N atoms to Na ion.

Table 1: Diffusion coefficients of DME, FSA, and Na in dilute (10%) and concentrated (40%) systems (10^{-10} m²/sec).

7.6	7.2
3.3	3.2
	7.6 3.3

The diffusion coefficient of DME decreased to ca. 1/4 in superconcentrated system, while those for Na and FSA decreased by about a half (Table 1). This result indicates the existence of a diffusion path of Na ion, which differs from the conventional vehicular type mechanism. As for such an extra diffusion process, we have newly found ligand (solvent/anion) exchange reactions (Fig. 2).



Fig. 2: Snapshots of Na ion diffusion accompanying ligand exchange reactions.

The rates of ligand exchange reactions were evaluated via number of associated/dissociated solvents/anions to Na ions averaged over 20 ps. The reaction rates for 40% and 10% systems were 0.019 (/ps) and 0.010 (/ps), respectively, implying roughly twice as frequent ligand exchange reaction in superconcentrated system.

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First-principles Study of Magnetic Materials

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Development of new strong magnet compounds have been attracting interests not only as a fundamental science but also for technological importance. Recently, NdFe₁₂N has been successfully synthesized as a film, and it was shown that the compound has larger saturation magnetization and anisotropy filed than Nd₂Fe₁₄B [1]. However, this compound is thermodynamically unstable, and it is necessary to substitute a part of Fe atoms with another element. Various elements, such as Ti, V and Si are known to stabilize the bulk phase.

In the present work, we study $NdFe_{11}M$ for M=Ti, V, Cr, Mn, Co, Ni, Cu and Zn. We have performed a first-principles calculation in DFT-GGA using QMAS code. Nd-4f electrons are treated as open-core. We found that M=Ti and Cr at the 8i site have negative formation energy. This suggests that the system is stabilized by Ti and Cr, which is consistent with experimental observation. We also found that M=Co has negative formation energy. Figure 1 shows the

magnetic moment and the second order crystalfield parameter. The magnetic moment is substantially smaller in NdFe₁₁Ti compared to NdFe₁₂. This is because Ti is negatively spinpolarized, and local magnetic moment at surrounding Fe sites also changes. In the case of M=Co, on the other hand, the spin moment is comparable to or larger than that of $NdFe_{12}$. The crystal-field parameter is also similar to that of NdFe12. These results suggest that Co can be a good stabilizing element in terms of structural stability and magnetization. The would have uniaxial system strong magnetocrystalline anisotropy by interstitial nitrogenation.

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Fig. 1: Magnetic moment and crystal-field parameter in NdFe₁₁M.