Part III

Beyond Density-Functional Theory
The main purpose of this project is to develop *ab initio* accurate schemes applicable to electronic structure calculation of strongly correlated electron systems that are known to hamper applications of conventional *ab initio* approaches such as the density functional theory (DFT). The second purpose is to apply the developed methods to challenging issues in condensed matter physics.

Among others, by utilizing a hierarchical energy structure of strongly correlated electron systems, we have developed an *ab initio* downfolding scheme called multi-scale *ab initio* scheme for correlated electrons (MACE) to make it possible understanding electronic properties of strongly correlated electron systems. In the scheme of MACE, we first calculate the global band structures for target materials, in which the high energy electrons far away from the Fermi level do not contain strong correlations effects and allows the conventional DFT. This part can be performed by the local density approximation (LDA) in the DFT, or alternatively the GW method. Then, we eliminate high-energy degrees of freedom by using the constrained random-phase-approximation (cRPA) method and obtain the low-energy effective model. To solve the *ab initio* low-energy effective models, we use various low-energy solvers such as many-variable variational Monte Carlo method and cluster extensions of the dynamical mean-field theory, which properly take into account both spatial and dynamical quantum fluctuations. This scheme has made it possible to clarify electronic properties of strongly correlated electrons accurately by low computational load. In this project, we have developed dimensional downfolding method, a method to treat dynamical screened interaction, and implemented to treat the spin-orbit interaction in the scheme. The applications include high-temperature superconductors including the iron-based, cuprate and fullerene superconductors and other superconductors such as aromatic and nitride compounds. We have also applied to organic conductors, alkali-cluster-loaded-zeolites, and systems with strong spin-orbit interaction such iridium oxides. We have also made progress in analyzing the experimental data of photoemission experiments on materials such as high-$T_c$ superconductors by the collaboration of experimentalists and theory group. Below, some of our achievements in our project are described.

(1) Mechanism of superconductivity in iron-based superconductors [2011-1), 2012-4), 2014-4)]

In iron-based superconductors, although it is believed that electron correlations and orbital degrees of freedom play key roles in stabilizing high-temperature superconductivity, their roles are not fully understood yet. To clarify microscopic mechanism of superconductivity in iron-based superconductors, it is necessary to evaluate strength of interactions in an *ab initio* way and it is also necessary to seriously examine the effects of electronic correlations. To challenge these issues, we employ *ab initio* downfolding scheme called multi-scale *ab initio* scheme for correlated electrons (MACE). We apply this method to the iron-based superconductors [1-4]. As a result, we show that the calculated magnetic order was shown to correctly reproduce the experimental material dependences [2,3]. By extending these normal state studies, we show that superconductivity emerges in the *ab initio* model of an electron-doped iron-based superconductor LaFeAsO in essential agreement with the experimental results [4]. The pairing satisfies gapped $s\pm$ symmetry and the specific orbital
(X2-Y2) is shown to play a key role in stabilizing the superconducting phase as well as the antiferromagnetic phase. Then, we find a one-to-one correspondence between superconductivity and enhanced uniform charge fluctuations. Similar one-to-one correspondence is also found in the Hubbard model [5], which is one of the simplest models for cuprates. Despite many differences between iron-based superconductors and cuprates, our study suggests that the enhanced uniform charge fluctuations play a key role in stabilizing the superconductivity in both materials.


(2) Ab initio studies of iridium oxides [2012-2), 2014-3), 2014-3])

Iridium oxides offer several different aspects of the interplay between the spin orbit interaction and the electron correlation. We have studied there different families of compounds as detailed below:

Ab initio analyses of A2IrO4 (A=Sr, Ba): Effective Hubbard-type models for Ir 5d t2g manifolds downfolded from the global band structure are solved based on the dynamical mean-field theory. The results for A=Sr and Ba correctly reproduce paramagnetic metals undergoing continuous transitions to insulators below the Néel temperature. These compounds are classified not into Mott insulators but into Slater insulators. However, the insulating gap opens by a synergy of the Neel order and significant band renormalization, which is also manifested by a 2D bad metallic behavior in the paramagnetic phase near the quantum criticality.

Topological properties of R2Ir2O7: We have theoretically shown that an emergent two-dimensional metal embedded in the bulk insulator is realized at a magnetic domain wall of R2Ir2O7. The domain wall has long been studied as ingredients of both old-fashioned and leading-edge spintronics. The domain wall here, as an interface of seemingly trivial antiferromagnetic insulators, emergently realizes a functional interface preserved by zero modes with robust two-dimensional Fermi surfaces, where pyrochlore iridium oxides proposed to host condensed-matter realization of Weyl fermions offer such examples at low temperatures. The
existence of ingap states pinned at domain walls, theoretically resembling spin/charge solitons in polyacetylene, solves experimental puzzles observed in R2Ir2O7 with rare earth elements R. The domain wall realizes a novel quantum confinement of electrons and embosses a net uniform magnetization, which enables magnetic control of electronic interface transports beyond semiconductor paradigm.

Studies on \textit{ab initio} effective low-energy Hamiltonian of iridium oxide Na$_2$IrO$_3$: The model has been reduced to an effective spin model on a honeycomb lattice by the strong coupling expansion. We have shown that the \textit{ab initio} model contains spin-spin anisotropic exchange terms in addition to the extensively studied Kitaev and Heisenberg exchange interactions, and allows us to describe the experimentally observed zigzag magnetic order, interpreted as the state stabilized by the antiferromagnetic coupling of the ferromagnetic chains. Possible routes to realize quantum spin liquids from existing Na2IrO3 have been proposed.

(3) Electron-phonon interaction implemented in the low-energy solver [2014-1]

We have developed a variational Monte Carlo (VMC) method for electron-phonon coupled systems. We propose a variational wave function with a large number of variational parameters, which is suitable and tractable for systems with electron-phonon coupling. In the proposed wave function, we implement an unexplored electron-phonon correlation factor, which takes into account the effect of the entanglement between electrons and phonons. The method has been applied to systems with diagonal electron-phonon interactions, i.e., interactions between charge densities and lattice displacements (phonons). As benchmarks, we compare VMC results with previous results obtained by the exact diagonalization, the Green function Monte Carlo method and the density matrix renormalization group for the Holstein and Holstein-Hubbard model. From these benchmarks, we show that the present method offers an efficient way to treat strongly coupled electron-phonon systems.

(4) Ca$_4$Al$_2$O$_6$Fe$_2$As$_2$ superconductor [2011-2]

It was pointed out in the early stage of iron-based superconductor research that the transition temperature has strong correlation with the bond angle between Fe and anion atoms, \( \alpha \). Ca$_4$Al$_2$O$_6$Fe$_2$As$_2$ is known for the smallest \( \alpha \) among iron-based superconductors. Our first-principles calculations clarified that the number of the Fermi surfaces around the Gamma point is smaller in Ca$_4$Al$_2$O$_6$Fe$_2$As$_2$ than that in LaFeAsO. As \( \alpha \) is hypothetically increased, the state 0.5 eV below the Fermi level, having xy character, is pulled up. It crosses the Fermi level, and a hole-like Fermi surface appears. As \( \alpha \) is increased further, the orbital energy becomes equal to that of the degenerate point at 0.2 eV, and band rearrangement takes place. The present result suggests that \( \alpha \) affects the superconducting transition temperature through the change in the Fermi surfaces.

(5) Aromatic compounds [2011-3]

It was reported experimentally that aromatic compounds such as picene and coronene become superconducting by alkali-metal doping. We have carried out density-functional calculation of picene and coronene. We found that pristine compounds are gapful. The conduction band consists of LUMO and LUMO+1 of the isolated molecules. In potassium-doped picene, the intralayer site is more stable than the interlayer site.

The LDA+DMFT method is widely used as a standard tool for correlated materials. The self-energy is approximated to be local in DMFT, and the Hubbard-$U$ is assumed to be static in the usual scheme. We have developed a LDA+DMFT scheme to treat dynamic $U$, and applied the technique, combined with the constrained RPA, to BaFe$_2$As$_2$. The dynamic $U$ effect enhances the electron correlation effect, and the system becomes strongly correlated as hole carriers increase. We have also proposed a scheme to renormalize the dynamic $U$ effect into one-body term of the Hamiltonian. We also studied the competition between the non-local self-energy effect and dynamic $U$ effect in the GW approximation. Application to SrVO$_3$ shows that the quasiparticle bandstructure is over renormalized when k-dependence of the self-energy is neglected. It is partially cancelled by the static $U$ approximation. In order to include both k-dependence of the self-energy and dynamic $U$ effect, we have developed ab-initio GW+DMFT scheme and applied the method to SrVO$_3$.

(7) Pyrochlore compounds [2012-7]

We have implemented relativistic DFT scheme based on the two-component spinor formalism in the QMAS code, and improved numerical convergence for the self-consistent calculation by changing a charge-mixing scheme, implementing penalty function for the spin moment, etc. We have applied the method to a pyrochlore oxide Cd$_2$Os$_2$O$_7$, and found that the material is an antiferromagnetic insulator in the LDA+$U$+SO with a reasonable value of $U$. The all-in/all-out magnetic order is the most stable state, in consistent with experimental observation. The single-ion anisotropy is comparable to the exchange coupling, and is stronger than the Dzyaloshinskii-Moriya interaction. In Y$_2$Mo$_2$O$_7$, on the other hand, there is a peculiar competition between magnetic states. The effective spin interactions are distinct from the simple Heisenberg form and strongly spin anisotropic in spin space.

(8) Rare-earth permanent magnet [2013-3, 2015-2]

Large magnetization and high coercivity are required for strong permanent magnets, and the latter has positive correlation with magnetocrystalline anisotropy. In order to search for new permanent magnet compounds, we have studied NdFe$_{11}$TiN by first-principles calculations using QMAS code. Interstitial nitrogenation increases electron density between Nd and N.
Feeling Coulomb repulsion from the electron density, the Nd-f electrons are extended in the ab directions. It induces uniaxial magnetic anisotropy. This has been confirmed semi-quantitatively by the calculation of the crystal-field-effect parameter, \( A_{20} \). Nitrogenation also enhances magnetization, whereas titanium substitution decreases magnetization substantially. These results suggest that NdFe\(_{12}\)N has better magnetic properties than NdFe\(_{11}\)TiN. Subsequent to our work, NdFe\(_{12}\)N film has been experimentally synthesized on top of W underlayer on MgO substrate, and it was found to have larger magnetization and higher anisotropy field than Nd\(_2\)Fe\(_{14}\)B for wide temperature range between room temperature and the Curie temperature.

**Developments of \textit{ab initio} technique for deriving low-dimensional models [2010-1]**

An \textit{ab initio} downfolding method is formulated to construct low-dimensional models. In addition to band downfolding by a constrained random phase approximation formulated for 3D models, screening away from the target layer (chain) is further involved. Eliminating the off-target degrees of freedom, namely, dimensional downfolding, yields \textit{ab initio} low-dimensional models.

The method is applied to derive a 2D model for the layered superconductor LaFeAsO, where interlayer screening crucially makes the effective interaction short-ranged and reduces the onsite Coulomb interactions by 10–20\% compared with the 3D model for the five iron-3d orbitals.

**Ab initio derivation of two-dimensional models of organic compounds [2012-1], [2012-6]**

With the above developed technique, we derived \textit{ab initio} two-dimensional extended Hubbard-type multiband models for EtMe\(_3\)Sb[Pd(dmit)\(_2\)] and \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \). The HOMO antibonding band of the Pd(dmit)\(_2\) salt has a triangular structure of the transfers with a one-dimensional anisotropy, in contrast to the nearly equilateral triangular structure predicted in the past extended Huckel results. The ratio of the larger interchain transfer \( t_b \) to the intrachain transfer \( t_a \) is around \( t_b/t_a \sim 0.82 \). The derived screened onsite interaction \( U \) and the largest offsite interaction \( V \) are \( \sim 0.7 \) and \( \sim 0.23 \) eV, respectively, for EtMe\(_3\)Sb[Pd(dmit)\(_2\)] and \( \sim 0.8 \) and \( \sim 0.2 \) eV for \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \). These values are large enough compared to transfers \( t \) as \( \sim 55 \) meV for the Pd(dmit)\(_2\) salt and \( \sim 65 \) meV for the \( \kappa\)-BEDT-TTF one, and the resulting large correlation strength \((U - V)/t \sim 10\) indicates that the present compounds are classified as the strongly correlated electron systems.

**Ab initio derivation of impurity models for iron-based superconductors**
We also studied *ab initio* impurity models to understand impurity effects in iron-based superconductors. Effective tight-binding Hamiltonians for the d bands of LaFeAsO with various transition-metal impurities such as Mn, Co, Ni, Zn, and Ru are constructed. Local electronic structures around the impurity are quantitatively characterized by their onsite potential and transfer hoppings to neighboring sites. We found that the impurities are classified into three groups according to the derived parameters: For Mn, Co, and Ni, their impurity 3d levels measured from the Fe 3d level are nearly, 0.3, −0.3, and −0.8 eV, respectively, while, for the Zn case, the d level is considerably deep as −8 eV. We also showed that, while excess carriers are tightly trapped around the impurity site (due to the Friedel sum rule), there is a rigid shift of band structure near the Fermi level, which has the same effect as carrier Doping.

**Fig.6:** Atomic geometry and anti-bonding HOMO Wannier functions for organic compounds. Left: EtMe3Sb[Pd(dmmit)2]. Right: κ-(BEDT-TTF)2Cu(NCS)2.

**Fig.7:** Left: Isosurface contours of maximally localized Wannier functions for dxy orbital of the impurity atom in La(Fe0.944Co0.056)AsO. Right: Comparison of electronic density of states (EDOS) for La(Fe0.944M0.056)AsO with M=Mn (red), Fe (green), Co (blue), and Ni (pink).

**12 Ab initio GW calculations for plasmon effects in the organic compound [2013-4]**

We developed an *ab initio* massively parallelized GW codes capable of being treated large systems. With this code, we performed calculations to study dynamical effects on an organic compound (TMTSF)$_2$PF$_6$. Calculated polarized reflectivities reproduce experimental plasma edges at around 1.0 eV and 0.2 eV along the a and b axes, respectively. These low-energy plasmons come out from the low-energy narrow bands energetically isolated from other higher-energy bands, and affect the low-energy electronic structure via the GW-type self-energy. Because of the quasi-one-dimensional band structure, a distinct plasmaron state is observed along the Y-G line and a large plasmon-induced electron scattering is found in the low-energy occupied states along the X-M line.
Superconductivity in alkali-doped fullerides (A3C60) is of great interest in particular due to its high transition temperature (Tc) that is the highest among molecular solids. In the phase diagram, the superconducting phase resides next to a Mott-insulating phase. While this situation is similar to that of cuprates, superconductivity in A3C60 is more surprising, since the gap function has an on-site s-wave symmetry for which one usually expects that local electron correlations causing the Mott-Hubbard transition severely suppress its Tc. To clarify this non-trivial pairing mechanism of A3C60, we performed first-principles studies based on superconducting density functional theory (SCDFT) and multi-energy ab initio scheme for correlated electron systems (MACE).

SCDFT is an extension of DFT for normal states to superconducting states. There, the Kohn-Sham equation is extended to the Kohn-Sham Bogoliubov-de Gennes equation from which the linearized gap equation is derived. In 2005, a kernel for the gap equation in SCDFT is formulated and has been applied to many conventional superconductors. There, it has been demonstrated that the experimental Tcs are accurately reproduced. Using the same kernel, we performed SCDFT calculations for K3C60, Rb3C60 and Cs3C60. We found that SCDFT systematically underestimates their Tc. This result suggests that we have to go beyond the standard Migdal-Eliashberg theory to understand high Tc in A3C60.

In MACE, we start with a derivation of an effective low-energy model for the t1u band around the Fermi level. Using the constrained random phase approximation (cRPA), we first evaluated the values of interaction parameters, such as the Hubbard U and the Hund’s coupling JH. We found that U is ~1eV, which is larger than the band width. Interestingly, U is larger for systems having higher Tc. This trend cannot be understood in terms of the Migdal-Eliashberg theory. We also found that the ratio JH/U is as small as 5%, which is much smaller than that of transition metal compounds. Thus there is an interesting possibility that the Hund’s rule can be inverted by the exchange coupling (JJT) due to the Jahn-Teller effect.

To estimate the size of JJT and investigate the subtle competition between JH and JJT, one needs to derive a low energy model with phonons. To this end, we formulated a new scheme, which we call constrained density functional perturbation theory (cDFPT). There, we can estimate the size of electron-phonon coupling and phonon frequencies in the effective Hamiltonian without including the screening effect of low-energy electrons.

We applied this new method to A3C60. We found that JJT is always larger than JH. In this situation, we can expect that intra-orbital pairing is significantly enhanced. We then solved the effective model by means of the extended dynamical mean field theory. We obtained a phase transition temperature that is in good agreement with the experimental value.

We extended SCDFT to take account of the dynamical structure of the screened Coulomb interaction and electron-hole asymmetry in the electronic structure. Through an application to fcc lithium under high pressures, we demonstrate that the new kernel in the gap equation improves the agreement between the calculated and experimentally observed $T_c$. [1]

(15) Development of HiLAPW code and its applications to Rashba surface systems and topological insulators [2013-8, 2014-8]

Aims of our group in this project are twofold: a development of new methods to enhance the capability of our density-functional-theory code HiLAPW and applications of the code to a variety of novel materials. One of the distinguished achievements in the methodological development is the proposal of an efficient and accurate formula for stress tensor calculations within the all-electron full-potential linearized augmented plane-wave (FLAPW) method. We have shown that the adoption of the Soler-Williams type basis in the FLAPW formalism results in a much simpler and robust expression of the stress tensor.

Applications of the HiLAPW code have been made mostly for novel materials and phenomena such as Rashba surface systems and topological insulators. The most impact result achieved is to clarify that the origin of weak Rashba-like band structure observed in Bi(111) thin films by an angle-resolved photoemission spectroscopy (ARPES) experiment is one-dimensional (1D) edge states of triangular bi-layer islands on the surface. Calculated band dispersions and spin-polarizations are consistent with the measured ARPES results. Another pronounced result can be seen in the electronic structure calculation for Au wires on Si(557) surface. It is shown that Rashba 1D metallic bands are formed not only from Au-6s orbitals but also Au-5d and neighboring Si-3p orbitals, leading to large spin-orbit origin out-of-plane spin polarization due to asymmetric electron density around the Au atoms by hybridization of orbitals with different parity. Peculiar electronic structure found in Bi overlayer on a three-dimensional topological insulator TiBiSe$_2$ has been successfully explained as a proximity effect due to spin-dependent hybridization between Bi layers and TiBiSe$_2$ surface.

(16) Single-component organic conductors [2014-12]

Conventional organic metals consist of more than two kinds of molecules. Their metallic nature is brought by charge transfer between different molecules. The discovery of the first single-component molecular metal Ni(tmdt)$_2$ (tmdt = trimethylenetetrathiafulvalenedithiolate) [1] has opened a new paradigm. Subsequently, various related compounds have been synthesized. They form a new class of materials named “single-component molecular metals (SCMM)”. We have studied electronic structures of several SCMM's by means of first-principles calculations [2]. First, we investigated the central metal dependence of the character of
electronic states around HOMO (or SOMO) and LUMO for isolated molecules. It has been found that the energy level of the pd\(\sigma\)(-) state shifts systematically depending on the central metal. We have also calculated electronic structures of their solid forms and revealed that band dispersion in the vicinity of the Fermi level for each solid reflects the electronic states of the corresponding isolated molecule. It should be noted that the relative energy level of the pd\(\sigma\)(-) state is one of predominant factors to control the electronic properties of the solid form.


(17) Exotic ferroelectricity in tetrathiafulvalene-p-chloranil [2014-7])

For the organic ferroelectric tetrathiafulvalene-p-chloranil (TTF-CA), theoretical calculations based on the Berry phase technique predicted large values of spontaneous polarization (8~10 \(\mu\)C/cm\(^2\)) [1,2] though experimental confirmation was difficult because of leakage current. Recently, Kobayashi et al. successfully obtained a value of 6.3 \(\mu\)C/cm\(^2\) [3]. In addition, they found that the polarization is more than 20 times larger compared with that of the point charge model and their directions are opposite [3]. We investigate details of the electronic structure and the origin of exotic ferroelectricity in TTF-CA in terms of effective charges and maximally-localized Wannier orbitals (MLWOs) from first-principles calculations.

In the crystal unit cell, there are two TTF molecules and two CA molecules forming two heterogeneous columns along the \(a\)-axis. There is a partial charge transfer between the TTF-HOMO and the CA-LUMO forming four electronic bands below and above the band gap [1]. Calculations were performed on the 90 K paraelectric structure (described as \(\lambda\)=0) and the 40 K ferroelectric structure (\(\lambda\)=1) [4] and their interpolations (\(\lambda\)=0.1, 0.2, … , 0.9). Molecular effective charges are defined as sums of Born effective charges for the constituent atoms. We have found that the molecular effective-charge-tensor components associated with the polarization show unusually large variations with \(\lambda\) and that two topmost occupied bands are responsible for these behaviors. We constructed MLWOs from the four bands in the vicinity of the band gap as well as from the two topmost occupied bands. The MLWOs from the four bands have TTF-HOMO-like or CA-LUMO-like shapes while those from the two bands look like linear combinations of the TTF-HOMO at the center and the CA-LUMOs on both sides. From analyses using these MLWOs, we propose a physically transparent picture to understand the mechanism of covalency-induced electronic polarization [5].


(18) Electron correlation in the Fermi-liquid system SrVO\(_3\) and the Hund’s metal SrMoO\(_3\) [2014-9])

A prototypical correlated system with d\(^1\) electronic configuration, SrVO\(_3\), has been studied by ARPES using high-quality single-crystalline films epitaxially grown on SrTiO\(_3\) substrates. Low (~60 meV) and high energy (~0.3 eV) kinks were observed in band dispersions, which we attribute to electron-phonon interaction and electron correlation, respectively. Through the Kramers-Kronig transformation of photoemission spectra in a self-consistent cycle, we obtained the electron self-energy over a wide energy range including the incoherent (lower Hubbard-band) feature. The d\(^2\) electron system SrMoO\(_3\) has also been studied by hard x-ray photoemission spectroscopy. In contrast to SrVO\(_3\), the spectra did not show a clear signature of
electron correlation in spite of the enhanced electronic specific heat. These apparently conflicting observations were consistently explained within the “Hund’s metal” scenario and were corroborated by DMFT calculations on the d² electronic configuration.

**19. Atom substitution effects in Fe-based superconductors [2013-9]**

Effects of transition-metal atom substitution for Fe atoms in Fe-based superconductors have been studied by ARPES measurements of Ba(Fe₁₋ₓMₓ)₂As₂ (M = Mn, Co, Ni, Cu, Zn). On the electron doping side (M = Co, Ni, Cu, Zn), the Fermi surface volume was found to be gradually deviated from prediction by the rigid-band model and concomitantly deep 3d states were formed. For M = Zn, the antiferromagnetic band structure of the parent compound was perfectly conserved, indicating that no electron doping occurred at all. We attribute this to the formation of a fully occupied Zn 3d band well below E_F and hence the stable valence of Zn^{2+}. As for the hole-doped side (M = Mn), too, hole doping did not occur, which we attribute to the stable half-filled Mn 3d shell, namely, the stable valence of Mn^{2+}.

**20. Fermi surfaces and superconducting gap anisotropy in Fe-based superconductors [2012-16], [2014-10], [2014-12], [2014-13]**

In order to elucidate the origin of the nodal superconducting behavior of BaFe₂(As₁₋ₓPₓ)₂, we have studied the Fermi surfaces and the superconducting gaps of this compound by ARPES. We did not find line nodes on the hole Fermi surfaces but a significant gap anisotropy on the electron Fermi surfaces. As for SrFe₂(As₁₋ₓPₓ)₂, which has a shorter c-axis parameter than the Ba compound, one of the three hole Fermi surface became more three-dimensional, and the superconducting gap showed different behaviors.

In iron-pnictide superconductivity, the interband interaction between the hole and electron Fermi surfaces (FSs) is believed to play an important role. However, KFe₂As₂ has three zone-centered hole FSs and no electron FS but still exhibits superconductivity. Our ultrahigh-resolution laser angle-resolved photoemission spectroscopy unveils that KFe₂As₂ is a nodal s-wave superconductor with highly unusual FS-selective multi-gap structure: a nodeless gap on the inner FS, an unconventional gap with “octet-line nodes” on the middle FS, and an almost-zero gap on the outer FS. This gap structure may arise from the frustration between competing pairing interactions on the hole FSs causing the eightfold sign reversal. Our results suggest that the A₁g superconducting symmetry is universal in iron-pnictides, in spite of the variety of gap functions.

We have also investigated the superconducting (SC)-gap anisotropy for several Ba-doped KFe₂As₂ samples using laser-based angle-resolved photoemission spectroscopy. We show that the SC-gap anisotropy and node positions drastically change with a small amount of Ba doping. Our results totally exclude a possibility of d-wave symmetry and strongly suggest that both spin and orbital fluctuations are important for the pairing interaction in the Ba-doped KFe₂As₂.

We performed a laser angle-resolved photoemission spectroscopy (ARPES) study on a wide doping range of the Ba₁₋ₓKₓFe₂As₂ (BaK) iron-based superconductor. We observed a robust low-binding energy (BE) kink structure (kink1) in the dispersion which is doping dependent whereby its energy peaks at the optimally doped level (x ~ 0.4) and decreases towards the underdoped and overdoped sides. We attribute this kink to electron-mode coupling in good agreement with the inelastic neutron scattering (INS) and scanning tunneling microscopy (STM) results on the same compound where a similar bosonic mode associated with spin excitations was observed. The relation between the mode energy (Ω) and the SC transition temperature (Tc) deduced from our laser ARPES data follow the universal relation deduced from INS and STM. In addition, we could resolve another kink at higher BE (kink2) showing less doping and
temperature dependence compared to kink1 and which thus may be of different origin.

**Selected Publication list**

**2010**


**2011**


**2012**


5) Yusuke Nomura, Merzuk Kaltak, Kazuma Nakamura, Ciro Taranto, Shiro Sakai, Alessandro Toschi, Ryotaro Arita, Karsten Held, Georg Kresse, and Masatoshi Imada, "Effective on-site

2013
6) Ryosuke Akashi and Ryotaro Arita, “Development of density functional theory for


2014


above the Fermi level: possible route to BCS-BEC superconductivity” Scientific Reports.,4:4109(2014)1-6

2015

Personal list of number of publications and invited talks

Masatoshi Imada: [Published papers in refereed journals] 31,
[Invited talks in international conferences] 26, [Invited talks in domestic conferences] 7
Takashi Miyake: [Published papers in refereed journals] 23,
[Invited talks in international conferences] 5, [Invited talks in domestic conferences] 7
Kazuma Nakamura: [Published papers in refereed journals] 17,
[Invited talks in international conferences] 7, [Invited talks in domestic conferences] 10
Ryotaro Arita: [Published papers in refereed journals] 20,
[Invited talks in international conferences] 25, [Invited talks in domestic conferences] 1
Tamio Oguchi: [Published papers in refereed journals] 42,
[Invited talks in international conferences] 7, [Invited talks in domestic conferences] 2
Shoji Ishibashi: [Published papers in refereed journals] 14,
[Invited talks in international conferences] 2, [Invited talks in domestic conferences] 13
Atsushi Fujimori: [Published papers in refereed journals] 12,
[Invited talks in international conferences] 10, [Invited talks in domestic conferences] 9
Shik Shin: [Published papers in refereed journals] 61, [Invited talks in international conferences] 20
Total: [Published papers in refereed journals] 220,
[Invited talks in international conferences] 102
1. Introduction

By employing the Green's-function techniques, the quantum diffusion Monte Carlo (DMC) simulations, several types of variational approaches, and the local-density approximation (LDA) or its refinements such as GGA to the density functional theory (DFT), we have studied various aspects of quantum many-body problems in condensed matter physics, based primarily on the first-principles Hamiltonian $H_{FP}$ to investigate the following two issues: (i) Some important physical concepts are so far established only by the analysis of model Hamiltonians. We assess their relevance in $H_{FP}$ by mainly using DMC, whereby we may find new physics by understanding the concepts more deeply. (ii) In the framework of DFT, all the many-body effects should originate from the universal energy functional, indicating that they should appear even in the homogeneous electron gas, in either its ground or excited states. With this recognition, we try to discover new concepts and/or quantum phases in the homogeneous electron gas by use of the Green's-function method not only in the many-body perturbation approach but also in the nonperturbative one like the GW scheme which can be applied to both Fermi and Tomonaga-Luttinger liquids. A reliable method for calculating superconducting transition temperature $T_c$ from first principles is developed along this line of research.

2. Summary

Here we mention a couple of topics as concrete problems in the first issue: (i) We have made DMC calculations to analyze the Kondo spin-singlet resonance state in the system of a proton embedded in the electron gas to find a paradigm shift in the metallic screening to a point charge due to the competition between the short-range spin-dependent interaction at the proton site and the long-range Coulomb interaction among metallic electrons, the latter of which is absent in the impurity Anderson model but present in $H_{FP}$. The exciton and biexciton physics is also investigated by DMC in the electron-hole bilayer system to establish a rich phase diagram.

As for the second issue, we have succeeded in the improvement on the GW scheme by inventing a good functional form for the three-point vertex function $\Gamma$, a key quantity in the self-consistent calculation of the electron self-energy $\Sigma$ in metals, to satisfy the conservation laws of not only the local electron number but also the total momentum. With use of this scheme, we have found an indication of a new exotic “light-fermion” phase in the 3D low-density electron gas. In the spin-charge separated 1D Luttinger liquid, we have discovered the concept of “pseudoelectron” by GW in combination with the Bethe Ansatz method.

Superconductivity in boron and carbon systems as well as electron-doped SrTiO$_3$ is investigated not only by theoretical calculations but also by collaboration with experimentalists.

More detailed explanations on the above topics, along with some other interesting subjects, are given in the next section.

3. Accomplishments

[1] Paradigm Shift in Metallic Screening to a Point Charge: Sharp Transition from Charge to Spin-Singlet Resonance State in the Proton Embedded Electron Gas (Takada, Maezono, and Yoshizawa)

According to Debye and Hückel in 1923, a point charge $+Ze$ in a metal is screened by the accumulation of metallic electrons (charge resonance as described by the linear response theory).
This concept of metallic screening is prevailing for a century, but if \( Z \) is not small, we need to consider the nonlinear effects in the screening, including the contribution from spin resonance. The contribution will be enhanced, if \( Z \) is a positive odd integer, such as \( Z=1 \) (case of a proton), in which a spin-polarized bound state might appear around the charged impurity site.

With the above idea in mind, we have investigated the problem of hydrogen impurity in metals, which attracts long attention from a technological point of view like hydrogen storage in solids. Its electronic state has been investigated in terms of a proton embedded in the electron gas, namely, an interacting many-electron system in a compensating uniform positive background, mostly by LDA to DFT, according to which we may summarize the situation as follows: At high metallic electron densities, it is well described by a bare proton \( \text{H}^+ \) screened by metallic electrons (usual charge resonance), while at low densities two electrons are localized at the proton site to form a closed-shell negative ion \( \text{H}^- \) protected from surrounding metallic electrons by the Pauli exclusion principle. However, no details are known so far about the transition from \( \text{H}^+ \) to \( \text{H}^- \) in the intermediate-density region.

As schematically shown in Fig. 1, we have obtained its complete picture, in particular, a sharp transition from \( \text{H}^+ \) screening charge resonance (CR) to Kondo-like spin-singlet resonance (SSR), the emergence of which is confirmed by the presence of an anomalous Friedel oscillation characteristic to the Kondo singlet state through DMC calculations with total electron number \( N \) up to 170. This picture enriches the paradigm for metallic screening to a point charge in the sense that, depending on \( Z \) and \( r_s \), defined by \( r_s = (3/4\pi n)^{1/3}a_B^{-1} \) with \( n \) the electron density and \( a_B \) the Bohr radius, the SSR with a very long Kondo screening length takes the place of the CR with a short Thomas-Fermi screening length. We also note that hydrogen is most stably embedded in the electron gas in the form of the SSR, implying that hydrogen is expected to reside at a site characterized by the local density of \( r_s \approx 4 \) in an inhomogeneous metal.

Incidentally, the accurate data obtained by DMC for the charge density distribution around the proton \( n(r) \) as a function of \( r_s \) are found to contribute much to the improvement on the exchange-correlation energy functional in the framework of GGA, a key quantity in the Kohn-Sham scheme in DFT.

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Symmetric electron-hole bilayer systems have been studied at zero temperature using DMC. A flexible trial wave function is used that can describe fluid, excitonic, and biexcitonic phases. We have calculated the condensate fractions and pair correlation functions for a large number of densities \( r_s \) and layer separations \( d \) and obtained the phase diagram as shown in Fig. 2. At small \( d \) we find a one-component fluid phase, an excitonic fluid phase, and a biexcitonic fluid phase,
and the transitions among them appear to be continuous. At \( d = 0 \), excitons appear to survive down to about \( r_s = 0.5 \) a.u., and biexcitons form at \( r_s > 2.5 \) a.u. A snapshot of the state is shown in each phase in Fig. 3.

![Phase Diagram](image)

**Fig. 2:** Schematic picture of the phase diagram expected for 2D electron-hole gas. Vertical (horizontal) axis means the inter-layer (mean inter-particle) distance given in Bohr unit. With fixing \( r_s \) to be 4.0, one gets such phase transition that from plasma phase, to exciton phase, and finally to biexcitonic phase, as our results confirm.

![QMC Snapshots](image)

**Fig. 3:** QMC snapshots capturing 2-component plasma, excitonic, and biexcitonic phases at the particle density, \( r_s = 4 \) bohr. Each phase appears as the spacing between layers, \( d \), decreases from three toward zero.

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The electron-gas model plays a very useful role in the discussion of the many-body properties of conduction electrons in metals. This model becomes even more important in low-density systems in which \( a_0 p_F \) is much smaller than unity \((a_0: \text{the lattice constant and } p_F: \text{the Fermi wave number})\), because the first-principles Hamiltonian \( H_{FP} \) in metals is reduced to this model in this limit, indicating that the universal behavior in the low-density metals can be captured by the investigation of the electron gas at low densities.

This model is completely specified by a single density parameter \( r_s \). In usual metals in which \( r_s \) is in the range 1 ~ 5, this model can be well treated by the appropriate combination of ring diagrams, ladder ones, and their exchange partners, but the situation becomes complex and difficult for \( r_s \) larger than 5.25 at which the electronic compressibility \( \kappa \) diverges and subsequently the dielectric catastrophe occurs in the sense that the static dielectric function in the long-wave-length region is negative. In close connection of this dielectric catastrophe, we have already discussed an anomalous behavior of the interatomic distance in the alkali fluid.
metals in the supercritical region, namely, for \( r_s \) between 5 and 8. We have also reported the calculated results on several physical quantities satisfying various sum rules, including the momentum distribution function \( n(p) \) and the one-electron spectral function \( A(p, \omega) \) in the same \( r_s \) region with employing the nonperturbative scheme of the GW method in which a very important improvement is made for the functional form of the three-point vertex function \( \Gamma \), so that the self-consistent calculation for the effective mass at the Fermi level \( m^* \) is made feasible for \( 5 < r_s < 8 \), as shown in Fig. 4.

Recently, we have applied this scheme to the even lower-density electron gas to find that \( m^* \) seems to vanish at \( r_s \sim 20 \), a new critical point associated with the problem of “light fermion”, concomitantly with the onset of strange behaviour in \( n(p) \) which is markedly different from that for \( r_s < 8 \), as shown in Fig. 5. We believe that physics behind these singular properties is the proximity to the instability of spontaneous electron-hole pair-formation excitations, whereby there are no (or very few) screening charges working for the electrons near the Fermi level. Note that \( m^* \) in the Hartree-Fock approximation in which the bare long-range Coulomb interaction is used in the calculation of the self-energy, becomes zero at the Fermi level, suggesting that the unscreened long-range Coulomb interaction induces a state with \( m^* \sim 0 \).

[4] Concept of “Pseudoelectron”: Generic Features of an Electron Injected into the Luttinger Liquid (Maebashi and Takada)

The concept of spin-charge separation plays a central role in describing low-energy physics near Fermi points in a 1D interacting electron gas, a typical example of the spin-1/2 Luttinger liquid (LL). This concept may be confirmed in real materials by the recent high-resolution angular resolved photoemission spectroscopy (ARPES) in which the one-electron spectral function \( A(p, \omega) \) can be directly measured in the wide range of momentum \( p \) and energy \( \omega \). Then, if \( p \) is not restricted to the region near \( p_F \), the linear spectrum approximation, usually adopted in the LL theory, is not sufficient in appropriately obtaining \( A(p, \omega) \). In fact, the effect of the nonlinear spectrum on \( A(p, \omega) \) has been intensively studied in recent years. According to those studies on integrable systems, \( A(p, \omega) \) has singularities for arbitrary \( p \) in proportion to
Fig. 6. Structural change of the pseudoelectron peak in the one-electron spectral function $A(p,\omega)$ for the Luttinger liquid (Yang-Gaudin model). Inset: The entire structure of $A(p,\omega)$ near $p_F$.

In pursuit of answers to those questions, we have carefully studied the one-electron Green's function $G(p,t)$ in momentum space and time and found that for $p \approx p_F$, its long-time asymptotic form is composed of three independent modes of power-law decay. Two of them correspond to well-known spinon and (anti)holon excitations, but the rest describes the mode of an electron-like particle (“pseudoelectron”) which may be regarded as an electron dressed with a “cloud” of low-lying spin and charge collective excitations. This pseudoelectron does not appear as a main structure in $A(p,\omega)$ for $p \approx p_F$ and never leads to a finite jump in $n(p)$. As $p$ goes away from $p_F$, the pseudoelectron structure gets broader, but with the further increase of $p$, it becomes less broad and eventually for $p \gg p_F$, it evolves as a main and divergent peak in $A(p,\omega)$ by swallowing the antiholon mode. Concomitantly, its dispersion relation approaches the one of a free electron, allowing us to regard the pseudoelectron as a free electron, but actually it is not quite, nor the Landau's quasiparticle, basically because this excitation is accompanied by power-law decay.

Those results clarify the generic feature of $A(p,\omega)$ in a 1D metal and answer the aforementioned two questions, as illustrated in Fig. 6.

[5] Survey of High-Tc Materials in Hard Semiconducting Boron Crystals (Shirai)

Since this century began, there was a big progress in the superconducting material research. Superconductivity was discovered among semiconductors, which was previously considered as only a theoretical interest. As a breakthrough, superconductivity was discovered in a boron crystal at high pressures. Since then, discovery of superconductivity followed in many semiconductors and now researchers are convinced that even phonon-mediated superconducting mechanism can yield high-$T_c$ superconductors, namely, above 40K. In this line of progress, boron crystals occupy a special position. These crystals are mechanically hard materials, suggesting strong electron-phonon interactions. Their light masses are also desirable for high-$T_c$
superconductors. In fact, there are many theoretical predictions to demonstrate high $T_c$ for boron and related compounds, including hypothetical ones (Table I). Then the main concern of experimentalists is how to prepare these structures or heavily doped samples.

The mission of this theoretical study is to devise suitable methods of synthesizing boron and its compounds in order to achieve high $T_c$. To this end, the DFT calculation of the phase diagram is of central importance, proposing ideas for material synthesis to experimentalists. This report includes the experimental results in accordance with our proposals. Lastly, we emphasize another role of this study as stimulating a search for new mechanisms of superconductivity in low-carrier-density systems.

$$N(E_f) \text{ [eV]}$$

\begin{tabular}{|l|l|l|l|l|l|l|}
\hline
Crystal & $N(E_f)$ & $\langle \omega \rangle$ & $\lambda$ & $\mu^*$ & $T_c$ (K) & References \\
\hline
B (fcc) & 0.15 & 107 & 0.39-0.53 & 0.09-0.13 & 5-15 & Papaconstantopoulos, 2002 \\
B (α-Ga) & 0.02 & 124 & 0.38 & 0.12 & 6 & Ma, 2004 \\
B (bct) & 0.009 & 97 & 1.02 & 0.17 & > 50 & Bose, 2005 \\
α-B & 0.24 & 65.8 & 0.81 & 0.1 & 36.7 & Calandra, 2004 \\
B$_{12}$CBC & 0.03 & 105 & 0.39 & 0.10 & 4.4 & Xiang, 2004 \\
BC$_5$ & 0.12 & 67.4 & 0.89 & 0.1 & 45 & Calandra, 2008 \\
Li$_x$BC & 0.23 & 58 & 1.5 & 0.09 & > 40 & Rosner, 2002 \\
\hline
\end{tabular}

Table I. Prediction of $T_c$ for boron and boron-related compounds

Strategy of high $T_c$ superconductors

In this study, we place the following three strategies as the basis of searching high-$T_c$ superconductors: (i) Use of high pressure. Almost all materials become metals under high pressure. Hence, high-pressure method is the most reliable method for obtaining superconductivity. (ii) Heavy doping. Currently, superconducting semiconductors are mainly prepared by doping method in more conventional processes. (iii) Use of compounds as an alternate method for doping. Heavy doing is very difficult when the amount of doping exceeds ten at.%. We expect appropriate form of compounds as playing a similar role as MgB$_2$.

Theoretical and experimental achievements

(a) Superconductivity under high pressure

When superconductivity was first discovered for β-rhombohedral (β-R) boron at $T_c$~6K, the transition occurred at a very high pressure (~160GPa). At that time, there was no phase diagram for boron and we did not know the structure at high pressures. Accordingly, our first mission was to predict phase diagram of boron. After completing this calculation, we found that α-rhombohedral (α-R) boron is stable at high pressures (see, Fig. 7). By collaborating with experimentalists, we made a plan to search superconductivity of α-R boron at high pressures. The merits of studying α-R boron are its controllability of defect states and its simple structure, which is advantageous for theoretical work.

After several-year survey, Shimizu et al. succeeded in observing superconductivity for α-R boron at high pressures of ~160GPa. Although $T_c$ of ~6K is not so high, this discovery yielded significant contribution to
superconductivity research. We showed that the metallic transition occurs at around 130GPa, and surprisingly the original structure of $\alpha$-R boron is retained up to 200GPa. This is unusual. Usually, for example, for Si, the crystal first undergoes phase transition to metallic structure (hexagonal), and then exhibits superconductivity. For the case of boron, superconductivity occurs even with retaining the original structure. The mechanism of metallization for this case is band overlap. Band bowing of the conduction bottom is the cause of this overlap.

(b) **Superconductivity by doping method**

Li doping for $\alpha$-R boron is a promising candidate. However, in spite of twenty-year efforts of experimentalists, no success has been obtained. The problem lies at difficulty in doping for $\alpha$-R boron. For $\beta$-R boron, on the contrary, Li doping is possible, but no metallic behavior is observed. Our study for doping based on phase-diagram calculation explains why the results are not as we expected. For $\beta$-R boron an intrinsic feature of geometrical frustration prevents the crystal from undergoing metallic transition. For $\alpha$-R boron, there is no such difficulty. Instead, its strong covalency prevents us from achieving heavy doping. At normal conditions, we predicted the solubility limit of Li at almost 0.1 at.%. This doping level is marginal for $\alpha$-R boron to exhibit superconductivity. Very recently, Kimura’s group succeeded in obtaining Li-doped $\alpha$-R boron at around this level, and showed superconductivity ($T_c$~5K). This is consistent with our prediction.

(c) **Compounds superconductivity**

The above approaches brought about superconductivity for $\alpha$-R boron, but $T_c$ is not so high as predicted. The main problem lies at the currently obtained carrier concentrations. For high-pressure experiment, the conduction and valence bands touch only slightly. For Li-doped $\alpha$-R boron, doping level of Li is only 0.1 at.%. We need as high doping level as 10 at.%. This limit could be lifted by using appropriate compounds. Theoretically, B$_{13}$C$_2$ is ideal for this purpose. This compound is predicted as metal without doping, and the predicted $T_c$ is about 37K. Unfortunately there is thus far no sign of superconductivity, and even of metallic behavior. The discrepancy between this fact and theory is a long-standing issue for this compound. We have solved this problem in terms of the effect of intrinsic defects of special type. Without controlling these defects metallic behavior cannot be achieved. A proposal for defect control is under consideration.

d) **Prediction of $T_c$**

For $\alpha$-R boron under conditions of doping or high pressure, the carrier concentrations are as low as $10^{21}$cm$^{-3}$. Our prediction for $T_c$ by the DFT calculation is exceedingly low, less than 1mK, while experiment somehow achieved ~5K. This big discrepancy says that the present predictability of $T_c$ for low-carrier concentrations is not reliable. In particular, the co-existing of electrons and holes complicates the problem. Solving this is still a challenge for theory.

**Summary and outlook**

Our predictions for metallic behavior of boron compounds have led experimentalists to sound way for finding superconductivity. The currently obtained $T_c$ is less than 10K, which is, however, by no means the intrinsic limit; it is just due to the preparation conditions presently feasible.

Our study is still being continuing and the on-going subjects are:

1) Hydrogenation of $\alpha$-tetragonal boron. One idea of solving defect states is passivation of defects by hydrogen incorporation. Recently, hydrogenation for $\alpha$-tetragonal boron has been succeeded by Ekimov’s group. It is a promising candidate for high-$T_c$ superconductors.
2) Control of boron carbide. The problem of $\text{B}_{13}\text{C}_{2}$ is frustration. High pressure synthesis has potential to resolve this. Recently, Manghnani has succeeded in compressing $\text{B}_{13}\text{C}_{2}$ by more than 10%. This has potential to have metallic behavior.

3) Li doping to $\alpha$-R boron. Currently, the solubility is around 0.1 at.%. However, by using high-pressure technique, we predict to achieve several at.% and accordingly high $T_c$.

[6] Superconductivity in Pseudoferroelectric Crystals: Case of $n$-doped SrTiO$_3$ (Sakurai and Takada)

Superconductivity near the ferroelectric quantum critical point is an intriguing issue of research and from this perspective, strontium titanate (STO: SrTiO$_3$) and its derivatives such as Ca$_x$Sr$_{1-x}$TiO$_3$ attract attention in recent years. STO is a widely used perovskite oxide with a band gap of 3.2 eV and is close to a displacive-type ferroelectric transition. When doped with substituting Nb for Ti or removing oxygen, the sample shows metallic behavior. Below 0.5 K, it exhibits superconductivity where the carrier density dependence of the critical temperature $T_c(n)$ has a dome shape, as is the case in high-$T_c$ cuprates. In 2013, Behnia’s group observed superconductivity even at $n=5.5\times10^{17}$ cm$^{-3}$ in oxygen-deficient samples. They also discovered another $T_c$ dome in the doping range lower than previously achieved in Nb-doped sample.

Based on the microscopic Hamiltonian $H$ containing the single-band pairing interaction in the ferroelectric displacive soft phonon mechanism in the long-range dielectric formalism, we have made an ab initio calculation of $T_c$ in the Kirzhnits-Maksimov-Kohmanskii scheme for the superconducting gap equation with determining the Coulomb pseudopotential $\mu'$ from first principles. In considering $H$, the one-electron dispersion is assumed to be parabolic with an effective mass $m^*$. With the values of parameters in $H$ taken from experiments, the $T_c$ dome observed in Nb-doped samples (i.e., in higher doping range) is reproduced well as shown in Fig. 9. We also find that a trend in $T_c$ for oxygen-deficient sample (i.e., lower doping) is captured by using a smaller $m^*$, which agrees with measurements, and a smaller phonon frequency, indicating the approach to a ferroelectric transition.

[7] Superconductivity in Graphite Intercalation Compounds: Case of BaC$_6$ (Takada and Sakurai)

Very recently, Tanigaki’s group succeeded in observing superconductivity in Ba intercalated graphite. The observed $T_c$~65mK is much lower than the value of 0.23K in the Eliashberg theory. In terms of Takada’s standard model for superconductivity in graphite intercalation compounds (GIC) in which the 3D interlayer band with a spherical Fermi surface superconducts, $T_c$ is also calculated to be about 0.2K. In order to investigate the reason for this discrepancy between theory and experiment, the band-structure calculation is done to find that the Fermi surface for the interlayer band in BaC$_6$ is not spherical but truncated, as seen in Fig. 10, due to the smaller
Brillouin zone for the system of large \(d\). By including this effect of truncation and also that of core polarization of Ba, which is very important in the polar-coupling mechanism in our standard model for GIC superconductors, we have successfully reproduced the observed \(T_c\).

[8] Non-Additivity in Metallic Tri-Wire Binding (Maezono)

We have investigated the non-additive contribution to the binding energy of three metallic wires modeled by 1D homogeneous electron gases. The three-wire contribution is evaluated in the equilateral triangle geometry by subtracting the bi-wire interaction energies from the total energy of the tri-wire configuration. As shown in Fig. 11, the three-wire contribution scales according to the power law \(\delta E \sim d^{-a}\) (\(d\) being the wire separation) with the exponent \(a\) being smaller than 3 and slightly increasing with \(r_s\) from 2.46 at \(r_s = 1\) to 2.91 at \(r_s = 10\), where \(r_s\) is the density parameter of the 1D electron gas. We find that the contribution falls off quite slowly, implying that it could be physically important.

Fig. 11; Asymptotic behavior of the bi-wire interactions \(u_2\) (left panel) and the non-additive contribution \(u_3\) (right panel) at \(r_s = 3.0\)

[9] Molecular Crystal Polymorphism (Maezono)

The prediction of molecular crystal polymorphism is one of the most challenging topics for current first principles electronic structure calculations. We have revisited our previous DMC simulation of p-DIB (para-Diiodobenzene) molecular crystal polymorphism to see how finite size errors affect the prediction of the polymorphism. We performed a significantly larger DMC calculation with a 1\(\times\)3\(\times\)3 simulation cell and a DFT nodal surface obtained from the PBE.
functional in the GGA to DFT. It was found that the resulting polymorph stability is still consistent with experiment, while standard DFT approaches failed (see, Fig. 12).

Fig. 12: Two possible polymorphs of p-DIB (para-Diiodobenzene). Conventional DFT cannot predict the correct stable structure, α, but our QMC has been confirmed to predict it.

[10] Superconductivity in a Correlated $E\otimes e$ Jahn-Teller System (Takada and Maebashi)

The competition of electron-phonon (e-ph) and electron-electron (e-e) interactions in the mechanism of superconductivity is an old issue in strongly correlated systems and it has been investigated mostly in a single-orbital system, like the Hubbard-Holstein model in which the e-ph interaction enhances charge fluctuations, inducing an s-wave superconductivity in the vicinity of CDW, whereas the e-e interaction works oppositely, leading to a d-wave superconductivity near SDW.

Here we add a further complication to this correlated and strongly phonon-coupled system by including the orbital degree of freedom. More specifically, we consider a 2D square lattice with each site made of an $E\otimes e$ Jahn-Teller (JT) center. At each center, we also consider the e-e interaction in an appropriate way to make this JT crystal as a prototype of the charge-spin-orbital complexes with the Hamiltonian $H=H_0+H_{ee}+H_{eph}$, where $H_0$ is the noninteracting part composed of the electron hopping term characterized by the nearest-neighbor and next-nearest-neighbor hopping integrals, $t$ and $t'$, respectively, with keeping the orbital symmetry and the degenerate-phonon term with the phonon energy $\Omega_0$. The orbital degree of freedom will be described by pseudospin for analogy to spin degree of freedom and the pseudospin symmetry is conserved throughout the crystal in this choice of $H_0$. Other terms, $H_{ee}$ and $H_{eph}$, consist of local-site terms written with the intra-orbital Coulomb interaction $U$, the Hund’s-rule coupling $J$, and the JT coupling $g$.

Due to the SU(2) symmetry in spin space and the conserved symmetry in pseudospin space, the Cooper pairing state can be specified by three quantum numbers; $S$ the total spin of the pair, $L$ the total pseudospin, and $L_y$ its $y$ component, making it possible to write the anomalous self-energy as $\Delta^{SLL_y}(k)$, where $k$ is a combined notation of crystal momentum $k$ and fermion Matsubara frequency. Because of the rotational symmetry around the orbital-$y$ axis, $L_y=\pm 1$ states are degenerate and thus we treat only either $L_y=0$ or $1$ here. The group theory determines the transformation property of $\Delta^{SLL_y}(k)$ in $k$ space; it transforms in accordance with $\Gamma$, one of the irreducible representation of the point group $C_{4v}$ ($A_1$, $A_2$, $B_1$, $B_2$, or $E$). The Pauli exclusion principle dictates that $\Delta^{SLL_y}(k)$ must be antisymmetric under two-electron interchange, indicating that $\Gamma$ must be $E$ for $(S,L)$ equal to either $(0,0)$ or $(1,1)$; otherwise $\Gamma$ must be either $A_1$, $A_2$, $B_1$, or $B_2$. With including this transformation property in $\Gamma$, we can easily write down the Eliashberg equation for $\Delta^{SLL_y}(k)$ at $T=T_c$ with the pairing interaction $V^{SLL_y}(q)$ containing the charge, spin, and orbital susceptibilities $\chi_c(q)$, $\chi_s(q)$ and $\chi_o(q)$, all of which are evaluated in the RPA with use of
the irreducible susceptibility $\chi^0(q)$.

In Fig. 13, the phase diagram at $T=0.02t$ is plotted in $U$-$g$ plane for the typical case of $t'=0.125t$, $U=8t$, $J=t$, and $\Omega_0=0.10t$ at half filling. Two boundaries, denoted by $L_I$ and $L_{II}$, indicates the lines where $\chi(q)$ and $\chi_s(q)$ diverge, respectively. In the close vicinity of these boundaries, those fluctuations are enhanced strongly enough to make the system enter into various superconducting phases, each labeled by $(\Gamma; S, L, L_y)$. Among them, we find $(E;0,0,0)$ a novel chiral p-wave pairing state $p_x(k)\pm ip_y(k)$ characterized by spin-singlet, orbital-singlet, and odd-parity in momentum space. This is a state very specific to the degenerate multi-orbital system and is induced by the cooperative effects of orbital and spin fluctuations that are enhanced by e-ph and e-e interactions, respectively.

The conservation of the pseudospin symmetry is assumed in this study, but it is not always the case. A tentative analysis indicates that perturbation breaking this conservation is expected to enhance $T_c$ for the iron pnictides, while it reduces $T_c$ very much for the vanadium oxides.

4. Research Members

Principal Investigator: Yasutami Takada (ISSP, U. Tokyo)
Co-Investigators (Kenkyū-Buntansha): Koun Shirai (Osaka U.)
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5. Publications and Invited Talks

Original Papers (58 papers in total)


Books and Chapters in Books (4 English articles and 2 Japanese articles in total)

Invited Talks (41 talks in total)
1) K. Shirai, K. Sakuma, and N. Uemura, “Defect states of boron carbide $B_{13}C_2$”, 18th International symposium on boron, borides and related materials (Honolulu, USA, 31 August-5 September 2014).
2) K. Hongo and R. Maezono, “Quantum Monte Carlo study of finite size effects in para-diiodobenzene molecular crystals”, XVIIIth International workshop on quantum system in chemistry, physics and biology (Paraty, Rio de Janeiro, Brazil, 1 December 2013)
4) Y. Takada, “Standard model for superconductivity in graphite intercalation compounds: Prediction of optimum $T_c$”, AIMR workshop on superconductivity and magnetism associated with geometry and dimensionality from organics to inorganics (Sendai, 17 May, 2013).

Organizers of International Conferences/Workshops (4 in total)
1) K. Shirai, The CECAM workshop “Modeling the Physical Properties of Clustering Crystals”, Lausanne, Switzerland, at the Ecole Polytechnique Fédérale de Lausanne (EPFL) from 4-6 November 2013 (Co-Chair).
2) Y. Takada, 7th ISSP International Workshop and Symposium “Emergent Quantum Phases in Condensed Matter –From topological to first principles approaches”, ISSP, U. Tokyo, Kashiwa, 3-21 June 2013 (Co-Chair).
Computational Design and Realization of Spintronics Materials

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1. Introduction

In this research project, to make a breakthrough in realizing spintronics as a practical electronics, we carried out collaborative research between computational design for spintronics and experimental verification. Concerning to the design for semiconductor spintronics, it has been desired to fabricate dilute magnetic semiconductors (DMS) with high Curie temperature ($T_C$). The main obstacle to realize high-$T_C$ DMS is low solubility of transition metal (TM) impurities in semiconductors. In order to overcome this difficulty, Sato proposed three possible directions of materials design (Sec. 2). Firstly, ‘co-doping’ method was proposed to control solubility of TM, and applied to the typical DMS GaMnAs. Secondly, it was shown that the spinodal decomposition in DMS could be used to organize nano-structures. Each nano-structure contains TM with high concentration, thus high-$T_C$ is expected. MgO-based DMS was picked up as typical example. Thirdly, new materials with high solubility of TM impurities were explored. LiZnAs- and GeTe-DMS were found to be good candidates for realizing high-$T_C$ DMS. In addition to the application of first-principles method to materials design as given above, it is also very important to develop computational method of electronic structure. Ogura developed screened-KKR method for band structure calculations to realize order-$N$ scheme (Sec. 3). The options to calculate magneto-optical properties and electric transport properties within the Keldysh formalism were also implemented.

Oda studied the topics on the search of metallic spintronic material (Sec. 4). In 2012, Oda started also studying a new topic under a collaborative research with the group of the non-scheduled project on “Development and application of the van der Waals density functional” (group of Ikutaro Hamada), in order to increase in sophistication about the method of electronic structure computations. In the latter collaboration, the method of van der Waals density functional (vdW-DF) was implemented in the code which has the option of imposing electric field (EF). As a result of the collaboration, a scheme which is applicable to magnetic materials was developed, and successfully applied some systems of magnetic molecules. Nozaki performed experimental demonstration concerning to the computational design for metallic spintronics, especially for the voltage control of magnetic anisotropy (Sec. 5).

In Sec. 6 a list of collaborators is given, and in Sec. 7 publications and invited talks related to this project are summarized.

2. Computational materials design for semiconductor spintronics

2.1. ‘co-doping’ method to control solubility of TM impurities in DMS

According to the first-principles prediction of Curie temperature of DMS, high concentration doping of TM impurities is required to achieve high-$T_C$. Due to the low solubility of Mn in
GaAs, GaMnAs usually shows phase separation into GaAs and MnAs. This is why non-equilibrium crystal growth technique is needed in fabricating DMS. Phase stability can be detected by calculating mixing energy $\Delta E$, which is defined as $\Delta E = E(Ga_{1-x}Mn_xAs) - (1 - x)E(GaAs) - xE(MnAs)$, where $E$ is the total energy of the system. Homogeneous GaMnAs, in which Mn distribute randomly at Ga sites, can be described by using the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) method. By definition, positive (negative) $\Delta E$ indicates phase separation (homogeneous mixing). Free energy of the system can be estimated by adding entropy term to the mixing energy and the temperature dependence of the free energy gives phase diagram of the system. In Fig. 1-(a), calculated phase diagram of GaMnAs is shown. In the calculation we did not suppose any ordered phase appeared. As shown in the figure, very large solubility gap is predicted in GaMnAs. In particular, spinodal region is wide, and $x = 0.2$ is already in the spinodal region at $T = 500$ (K). This reasonably explains difficulty of crystal growth of homogeneous GaMnAs. Li co-doping at the interstitial site changes the situation significantly as shown in Figs. 1-(b) and (c). Due to the lowering of $\Delta E$, solubility gap and spinodal region are reduced very much and high concentration doping of Mn becomes possible, e.g., even at thermal equilibrium at $T = 500$ (K), Mn can be doped up to 25% without phase separation. Similar co-doping effect is observed in GeCrTe co-doped with I.

Since the co-dopant Li behaves as a donor in GaMnAs, the hole carriers are compensated. Therefore, it is necessary to remove Li after the crystal growth. In order to show the possibility of low temperature annealing, we calculate diffusion barrier of interstitial Li in GaMnAs and by performing kinetic Monte Carlo simulations we estimated effective diffusion constant of interstitial Li in GaMnAs. It was found that binding energy between interstitial Li and substitutional Mn is rather small compared to interstitial Mn and substitutional Mn, therefore interstitial Li can diffuse rather long distance (~1 µm) during reasonable annealing time (~24 hours) with reasonable annealing temperature (~500 K) even with very high concentration of Mn (~30%).

### 2.2. Self-organization of nano-structures in DMS

In standard DMS systems, such as GaMnAs, InMnAs and so on, magnetic TM impurities are doped in non-magnetic semiconductors. Recently, ferromagnetic DMS systems without doping magnetic impurities attract scientific attention as $d^0$ ferromagnetism. Typical examples are Si- or Ge-doped K$_2$S, C- or N-doped CaO and SrO. We found that MgO could be ferromagnetic by doping N at O site or by introducing Mg vacancies. MgO-based DMS is interesting due to its sustainability and compatibility with existing spintronics devices. There are experimental verifications concerning to the $d^0$ ferromagnetism of MgO-based DMS. In contrast to the predicted low $T_C$, there are some experimental observation of room temperature ferromagnetism.
in 13% N-doped MgO and MgO with a few % Mg-vacancy.

We believe that this discrepancy between theoretical predictions and experimental observations is due to the spinodal decomposition in these systems. According to the calculations of effective pair interactions between N impurities in MgO, there are attractive effective interactions between N impurities. The effective pair interactions are also calculated to be attractive between Mg-vacancies. For the calculation of pair interactions, the generalized perturbation method formulated by Ducastelle and Gautier was employed. Due to these attractive interactions, nano-structure of self-organized and high concentration of N or Mg-vacancy is realized locally. Particularly, columnar structures appear under the layer-by-layer crystal growth condition (Fig. 2). Since the attractive interaction between Mg-vacancies are significant only for 2nd neighbors, the columnar nano-structures shown in the figure are simple cubic array of Mg-vacancies. We claim that this nano-structure formation also explains the conductivity, tunnel barrier and quantum oscillations of MgO-based magnetic tunnel junctions.

### 2.3. Search for new ferromagnetic DMS systems

There are several semiconductor systems which show large solubility of TM impurities. For example, GeTe, which is one of the typical IV-VI semiconductors, is known to accommodate Mn up to 50 % in thermal equilibrium. It is also known that GeTe has intrinsically p-type due to the Ge vacancies. Thus, Mn-doped p-type GeTe is promising as high-$T_C$ DMS. Actually, $T_C = 190$ K was observed in Mn-doped GeTe. In order to see how large $T_C$ can be expected, we calculated $T_C$ of GeMnTe as a function of concentration of Mn and Ge-vacancy. The electronic structure of GeMnTe with Ge-vacancies was calculated by using the KKR-CPA and magnetic exchange interactions between Mn were calculated by using the Liechtenstein’s formula. $T_C$ can be calculated based on the mean field approximation (MFA), random phase approximation (RPA) and Monte Carlo simulation (MCS). Among them the MCS gives exact $T_C$ within the numerical accuracy. According to the calculated DOS by the KKR-CPA, the GeMnTe system

![Fig. 2: Self-organization of Mg vacancies in MgO. The location of Mg-vacancies are indicated by blue points.](image1)

![Fig. 3-(a): Calculated effective exchange interactions between Mn in p-type GeTe as a function of distance for various concentrations of Ge vacancy. Mn concentration is fixed to 10 %.]  

![Fig. 3-(b): Calculated Curie temperature of Mn-doped p-type GeTe. Ge vacancy concentration is 20 %. MFA (black crosses), RPA (red pluses) and MCS (blue squire are employed for the calculations.](image2)
shows very similar electronic structure to GaMnAs, i.e., Mn-d states are located at the middle of host valence bands. Because of the strong hybridization, the states at the top of the valence bands, which are mainly Te-p states, show considerable amplitude of Mn-d states. The calculated exchange interactions are shown in Fig. 3-(a). Mn does not bring any carriers in GeTe, thus the system is insulating and the exchange interactions are negative (anti-ferromagnetic) due to the super-exchange interaction between Mn. The hole carriers originated from Ge-vacancies activate ferromagnetic interaction via the p-d exchange mechanism, and the interaction become positive. As shown in Fig. 3-(b), calculated $T_C$ shows maximum ($\sim 250$ K) at 40% of Mn concentration with 20 % Ge-vacancy. This $T_C$ is higher than the record in GaMnAs but lower than room temperature. We also calculated electronic structure and magnetism of Mn-doped Ge-Sb-Te ternary compound, which is known as phase change material, by using order-N KKR. For the calculations, we used KKRnano package developed by Juelich group. Local environmental effects in exchange interactions were investigated.

As another candidate of DMS where TM impurities can be doped up to high concentration, we propose LiZnAs compounds. This compound is a kind of derivative of GaAs, i.e., Ga$^{3+}$ ion is replaced with Li$^+$ and Zn$^{2+}$. Zn ion occupies cation site in Zinc Blende structure and Li ion locates at interstitial site. Since Mn$^{2+}$ is iso-electric to Zn$^{2+}$, we can expect high solubility. This was confirmed by the calculation of the formation energy. Since Mn$^{2+}$ is iso-electric to Zn$^{2+}$, we have to dope charge carriers to induce ferromagnetic interactions between Mn. One of the advantage of LiZnAs is that we can control charge carriers by changing Li concentration. By reducing (increasing) Li concentration, we can make LiZnAs p-type (n-type). As increasing the concentration of carriers, $T_C$ calculated by the MFA becomes positive (ferromagnetic). It was shown that both p-type and n-type doping could induce ferromagnetism. This is unique feature of the present system, because ferromagnetic n-type DMS is not common. According to accurate MCS shown in Fig. 4, $T_C$ reaches 100K with 15% Mn and 30% excess Li. This is higher than the $T_C = 34$ K of existing n-type ferromagnetic InFeAs. The carrier doping also affects phase stability of Mn-doped LiZnAs. The calculated mixing energy of LiZn$_{1-x}$Mn$_{x}$As indicates the phase separation into LiZnAs and LiMnAs. It was found that the mixing energy was reduced as increasing and decreasing Li concentration from stoichiometry. Therefore, the tuning of Li concentration contributes to two aspects of the fabrication of DMS, i.e., increasing $T_C$ and suppressing phase separation.

In addition to the development of computational materials design for semiconductor spintronics, Sato and Fukushima studied conventional calculation procedure of Hubbard $U$ parameter within the constrained-DFT scheme. In this scheme, $U$ is calculated as $U = E(N + 1) + E(N - 1) - 2E(N)$, where $E(N)$ is the total energy of $N$ electron system. In the case of Mn in GaN, $U$ was calculated to be 0.94 eV. By including the spread of the wave function, $U$ was corrected as 3.8 eV which agrees reasonably with the previously proposed value $U = 4$ eV.
3. Development of KKR-CPA code and order-\(N\) KKR method

Ogura developed the KKR-CPA package to calculate magneto optical properties such as magnetic circular dichroism, magnetic Kerr effects and so on. The method is based on the Kubo formula applied to the optical conductivity calculation. This method was applied to typical DMS systems such as CdMnTe and GaMnAs. It was re-confirmed that the ferromagnetism was strongly related to the existence of hole carriers in the valence bands.

Another important property of semiconductor spintronics materials is the electric conductivity, especially for magnetic multi-layered systems. For the simulation for spintronics devices, we have to treat large systems, therefore order-\(N\) method is indispensable. In the KKR method, we have a freedom to choose reference system. Normal choice is free space. Instead, we can use hypothetical array of repulsive potentials. Due to the exponential decay of the structure constants, we only have to include neighboring scattering sites in the Green’s function. Due to the tri-diagonal shape of the Green’s function, the calculation load becomes order-\(N\). We applied this method to the p-n junction of GaAs and calculated electric conductivity under the finite bias. For p-type (n-type) region, GaBeAs and GaSiAs were supposed. At both sides of junctions, Al leads were assumed. Keldysh Green’s function method within the KKR framework was also developed in order to calculate the electronic structure under the finite bias self-consistently. This formalism opens the way to calculate spin transfer torque.

4. Computational materials design for metallic spintronics

Concerned with the design of metallic spintronic materials, Oda studied on the magnetic state of magnetic thin films under the electric field (EF), with using the fully relativistic two-component pseudopotential first-principles electronic structure method based on the density functional theory (DFT). The program code developed in the project was based on the previously-developing house-made code. During the financed period, the new options of imposing EF were added and upgraded. As a result, though the results related with the material design are described later, efficiency of the program code was verified by successful computations. Moreover, thanks to the discussions with the members of the experimental group for metallic spintronic materials the study of this project was efficiently prompted and successfully realized a fruitful research result.

As a target of magnetic thin films, the magnetic anisotropy energy (MAE) which is extracted from the direction dependence of the total energies of the system was studied; particularly for the metallic thin film (vacuum/M/Fe/M(001), M=Pt, Pd), the magnetic junction film (MgO/Fe/M(001), M=Au,Pt), and double interface thin film (MgO/Fe/MgO) were investigated. In the metallic thin film, the semi-quantitative agreement with the available experimental data was obtained and the validity of computational method was confirmed. In the magnetic junction film, the EF effects of MAE on the systems of Pt substrate are larger than those of Au substrate. In the double interface thin film, both the large effect and non-linear behavior with respect to the EF of MAE were obtained, building up a first step to understanding the mechanism on voltage (bias)-effect in the experimental measurement. The guiding principles obtained in the project can be very useful to the design on EF effect for the metallic spintronic materials.

The research results of the EF effect on MAE are summarized to the following seven points.

1. In the two kinds of the junction films (MgO/Fe/M(001), M=Au, Pt), the magnetic anisotropy and its EF effect were investigated. We found that in the Pt system the EF effect become several times larger than those of the Fe system without the Pt layer.
2. Evaluating the MAEs and their variation with respect to the EF in the metallic magnetic thin
films (vacuum/M/Fe/M(001), M=Pt, Pd), we successfully explained the quantitative properties in the EF effect observed in experiments. Moreover, introducing a new quantity of MAE density for analyzing the EF effect of magnetic anisotropy, we successfully obtained the knowledge on the real space distribution contributed to the MAE.

3. We indicated that the MAEs and their EF effect can be changed by inserting the monoatomic layer of the elements (Au, Pt, Pd) at the interface between the metallic magnetic layer and the insulating layer, and successfully discussed the critical EF value at which the magnetic anisotropy transition occurs.

4. Discussing the problem of segregation effect for Au element by evaluating the MAE and its EF effect in the junction thin film, we obtained the very good agreement in conformity with the experimental result. Based on these results and the fact of the stable surface energy of Au layer, we obtained the probable guess that the segregation of Au frequently appears on the Fe layer when using the Au substrate in the experiment.

5. We obtained the discussions about the role of Co element at the interface of MgO/Fe by investigating the structural and electronic properties and the MAE in the junction film MgO/Fe(1-x)Co(x), etc. It was clarified that the Co element suppresses the stability of perpendicular magnetization, however, enhances the EF effect on MAE. From these results, the effectiveness of Co control in the magnetic material Fe(1-x)Co(x) was not clear.

6. Using the code of magnetostatic dipole-dipole interaction, which was developed during the project period, we found that the shape magnetic anisotropy induced by several Fe monoatomic layers was closely canceled out by the perpendicular magnetic anisotropy originated from the spin-orbit interaction. This theoretical fact was found to agree well with many experimental facts. The switching of magnetic anisotropy which is induced by EF was theoretically supported.

7. We investigated the MAE and its EF effect in the double interface MgO/Fe/MgO(001) and obtained the non-linear property in the EF variation of MAE. The MAE data calculated, the variation rate with respect to the EF, were in good agreement with the experimental data.

Here, as an example, details of the 7th research result are described. In Fig. 5, the MAEs are shown with respect to the EF. The important results are summarized to two points: obtaining the non-linear dependence of MAE and a good agreement with the experimental result on the EF variation rate of MAE. Property of the non-linear dependence was found to correlate with the number of electrons on the Fe atom at the interface which the EF was imposed on. In Fig. 6, we show the partial density of states (PDOS) projected to the 3d orbitals on the Fe atom at the interface, at the EF which minimized the MAE. We obtained the localized electronic states of Fe 3d orbitals just above the Fermi level. They were found to extend to the directions where the covalent bond was not formed at the interface, and also found to correspond well to the interface resonance state (IRS) observed in experiment.

Concerned with sophistication in the first-principles molecular dynamics with the option of EF, various options in the boundary condition of EF were successfully introduced. Concerned with development in the computational code, combining the MPI parallel computation with the
OpenMP parallel computation (implementing a hybrid parallel computation), we successfully obtained a speed-up in the execution. In order to utilize GP-GPU in application calculations in future, we also investigated the expected speed-up of the code.

Concerned with the research results in development, implementation, and verification of the van der Waals density functional (vdW-DF) method and in the application to magnetic system, the resulting data in the non-magnetic materials were confirmed to coincide with the previous data reported in past and the new functional of vdW-DF was proposed for magnetic materials. In the latter achievement, the application to practical magnetic materials was reported first time over the world. In the vdW-DF method, the options of atomic forces and cell stresses were introduced. For the verification calculations of argon, graphite, selenium, and solid carbon dioxide (dry-ice), we obtained good results. Concerned with magnetic systems, we also obtained systematically good results in the calculations of the pair of oxygen molecules and the solid oxygen. The new functional for vdW spin-polarized density functional method, which was developed and investigated for magnetic materials during this project, was not applied to so many systems. Therefore, it is necessary to increase the number of applications for development and verification of the functional. As a future problem of interface system, it may be interesting to clarify the effect of EF in the realistic materials where the vdW interaction is important.

Here, details of the results related with the application to magnetic material of the vdW-DF are described. The structural data of solid oxygen at ambient pressure is shown in Table 1. The results of LDA and GGA differ largely from the respective experimental data, however, these of vdW-DFs much improves the structural data. It is important that the extension to spin-polarized materials of vdW-DF is applied to both the study of solid oxygen under high pressure and the application of magnetic systems other than oxygen system to order to verify the effectiveness of vdW-DF.

Table 1. Crystal structure data, molecular binding energy, and magnetic energy of the solid oxygen at ambient pressure.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Volume (Å³/mole)</th>
<th>ΔE^{O2} (meV/mole)</th>
<th>ΔE^{mag} (meV/mole)</th>
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<tr>
<td>LDA</td>
<td>3.29</td>
<td>3.28</td>
<td>4.05</td>
<td>113.9</td>
<td>19.93</td>
<td>522</td>
<td></td>
</tr>
<tr>
<td>GGA(PBE)</td>
<td>4.59</td>
<td>3.93</td>
<td>5.05</td>
<td>122.1</td>
<td>38.54</td>
<td>41</td>
<td>95</td>
</tr>
<tr>
<td>vdW-DF</td>
<td>4.68</td>
<td>3.68</td>
<td>4.70</td>
<td>125.2</td>
<td>33.04</td>
<td>221</td>
<td>118</td>
</tr>
<tr>
<td>vdW-DF-GC</td>
<td>4.92</td>
<td>3.56</td>
<td>4.29</td>
<td>128.3</td>
<td>33.93</td>
<td>213</td>
<td>87</td>
</tr>
<tr>
<td>vdW-DF2</td>
<td>3.83</td>
<td>3.85</td>
<td>4.30</td>
<td>118.6</td>
<td>27.75</td>
<td>225</td>
<td>304</td>
</tr>
<tr>
<td>vdW-DF2-GC</td>
<td>3.91</td>
<td>3.88</td>
<td>4.36</td>
<td>119.9</td>
<td>28.56</td>
<td>209</td>
<td>251</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.403</td>
<td>3.429</td>
<td>5.086</td>
<td>132.3</td>
<td>34.85</td>
<td></td>
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</tr>
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</table>
5. Experimental demonstration of voltage-induced perpendicular magnetic anisotropy

5.1. Materials search for voltage control of magnetic anisotropy

Spintronic devices is expected as a promising green IT due to its low stand-by power based on the non-volatility of ferromagnetism. However, one of the technical challenges is the reduction in operating power. For manipulating spin states, we need to use electric-current application and it consumes high energy due to Ohmic dissipation. Therefore, voltage-control of magnetic properties will be a key technology for future spintronics to realize an ideal green IT with low stand-by and operating power.

One promising approach is the voltage-control of magnetic anisotropy (VCMA) in an ultrathin ferromagnetic metal layer. We first demonstrated this effect in all solid device consisting of Au / ultrathin Fe / MgO junction in 2009. VCMA effect can be induced by various mechanisms, such as charge screening induced spin-imbalance and modification in band structure, voltage control of interfacial oxidation state, Rashba spin-orbit coupling, ferroelectric switching of chemical bonding or strain and so on. In particular, carrier-mediated effect at the interface of ultrathin ferromagnetic metal and MgO has high potential for applications, however, we need further improvement in the amplitude of voltage effect.

To enhance the voltage effect we focused on the materials research for the buffer materials. We prepared single crystal junction structure of buffer material X (Pd or Ag)/ ultrathin Fe / MgO / Polyimide / ITO on single crystal MgO(001) substrate using molecular beam epitaxy. Magnetic property of the ultrathin Fe layer was investigated by magneto-optical Kerr effect under the bias voltage application between the buffer layer and top ITO electrode. For the case of Pd buffer, estimated surface anisotropy energy $K_{i,0}$ and the slope of the surface anisotropy energy change were 470 mJ/m$^2$ and 100 fJ/Vm, respectively. These are comparable to that observed in Au/ultrathin Fe/MgO junction. On the other hand, for the Ag buffer prepared at room temperature exhibits high $K_{i,0}$ of about 980 mJ/m$^2$ as shown in Fig. 7-(a). An example of the bias voltage effect on magnetic hysteresis curve is displayed in Fig. 7-(b) for the Fe thickness of 0.7 nm. Clear changes in the perpendicular anisotropy was observed and the slope of the anisotropy change reached 195 fJ/Vm. The VCMA effect should be controlled at the Fe/MgO interface, however, we found that the buffer material also has strong influence probably through the segregation or inter diffusion during the deposition or annealing process.

![Fig. 7: (a) Surface anisotropy energy as a function of Fe thickness in Ag / ultrathin Fe / MgO structure, and (b) example of VCMA effect observed in the junction with $t_{Fe}=0.7$ nm.](image-url)
5.2. Impact of under-layer materials on voltage-induced magnetic anisotropy change in CoFeB/MgO junctions

After the first demonstration of VCMA effect in the junction structure with buffer / ultrathin ferromagnet / MgO / Polyimide / ITO, we realized this effect in a magnetic tunnel junction structure. It is now one of the standard structures to investigate the VCMA effect through the TMR effect, however, experimental results, such as the amplitude of the VCMA change or even its sign, are often scattered between the research groups and theoretical predictions. In this study, we investigated the VCMA change in sputter-deposited-CoFeB/MgO junctions with different buffer layers of Ru and Ta.

Buffer/Ta(5)/Ru(0 and 5 nm)/Co16Fe64B20(1.4 nm)/MgO(2 nm)/Co16Fe64B20(10 nm) were deposited on thermally oxidized Si substrate by using DC and RF magnetron sputtering. Then, the films were micro-fabricated into magnetic tunnel junctions (MTJs) using electron-beam lithography and an Ar ion milling. The samples with Ta and Ru under-layers were annealed at 300°C and 200°C, respectively, to realize perpendicular spontaneous magnetizations in thin-CoFeB layers. We investigated the VCMA from TMR curves under in-plane magnetic fields. Sign of the bias voltage is defined with respect to the top thick-CoFeB electrode.

Figs. 8-(a) and -(b) shows the normalized in-plane magnetization curve determined from MR curves under positive and negative bias voltages. The polarities of voltage-induced perpendicular magnetic anisotropy change are opposite between MTJs with Ta and Ru under-layers. This feature was also confirmed through the voltage-driven FMR measurement.

As discussed above, VCMA effect should originate from the CoFeB/MgO interface, however, we observed clear changes in the VCMA even with the sign change. Possible origins are differences in the crystalline structure or intermixing condition at the CoFeB/MgO interface or difference in the spin-orbit strength in the underlayer may also affect on the electronic structures around the Fermi level in the CoFeB. We need further investigation to make these points clear.

Fig. 8: Magnetic field dependence of the normalized in-plane component of the magnetization estimated from TMR curves under different bias voltage conditions in CoFeB/MgO junctions grown on (a) Ta and (b) Ru under-layers.
5.3. Voltage control of magnetic anisotropy in a magnetic tunnel junction with MgO double barriers

An important technical issue of VCMA effect is to realize the large anisotropy change with keeping high thermal stability. Because of the interface effect, we need to use an ultrathin layer of the order of a few monolayers to observe the VCMA as discussed above. On the other hand, thermal stability of nano-sized magnetic bit depends on its volume, therefore, reduction in the thickness degrades the thermal stability. A magnetic tunnel junction (MTJ) with double MgO barriers is promising structure to solve this problem. Since the perpendicular anisotropy comes from the Fe/MgO interface, surface anisotropy can be doubled by using the MgO/Fe/MgO structure. This structure has been studied for the spin-torque based devices, but there was no report about the VCMA.

Fig. 9-(a) shows the detailed sample structure of double barrier MTJ prepared in this study. Here, middle FeB thin layer is the voltage-driven layer, and bottom thick Fe layer is a reference layer to detect the magnetization direction of FeB layer. If two MgO barriers are completely symmetric, first order term of the voltage effect could be cancelled by two interfaces, so top side MgO barrier was designed to be thinner than the bottom side one in order to introduce the asymmetry. Therefore, we can consider that the bias voltage is applied only at the bottom side MgO/FeB interface. However, the top MgO barrier plays an important role to give high perpendicular anisotropy to the FeB layer. Voltage effect on the perpendicular magnetic anisotropy was summarized in Fig. 9-(b).

Perpendicular magnetic anisotropy energy, $E_{\text{perp}}$ was evaluated from the bias voltage dependence of TMR curves with saturation magnetization value obtained from VSM measurement. The surface anisotropy energy, $E_{\text{perp,FeB}}$ under zero bias voltage was estimated to be about $300 \mu J/m^2$. This value is about 6 times larger than that obtained in our previous study (Au/FeCo/MgO structure) and about 1.5 times observed in MgO/CoFeB/Ta structure, thanks to the two FeB/MgO interfaces.

In the positive bias direction, where the depletion of electrons is induced at the bottom MgO/FeB interface, linear enhancement of the surface anisotropy energy was observed with the slope of $110 \text{ fJ/Vm}$. This is about 2 time larger than that observed in CoFeB/MgO/CoFeB/Ta MTJ. These results suggest that we can achieve large VCMA effect with keeping high thermal stability in the double barrier MTJs.

And another interesting feature observed in this sample is that the perpendicular anisotropy increases even under the negative bias direction. This feature was explained theoretically as an influence of charged interface by Oda. If we can control this nonlinearity intentionally by structural design, it has high potential to extend the availability of VCMA.

Fig. 9: (a) Sample structure of voltage-driven double barrier MgO-MTJ and (b) summary of voltage-induced surface anisotropy energy change estimated from TMR curves.
6. Collaborators

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7. Publications and Invited talks

Publications


16) M. Tsujikawa, S. Haraguchi, T. Oda et al., “A Comparative ab initio study on electric-field dependence of magnetic anisotropy in MgO/Fe/Pt and MgO/Fe/Au films”, J. Appl. Phys. 109 (2011) 07C107(1-3).


Invited Talks

2) M. Ogura, “First-principles calculation of the magneto-optical effects of magnetic semiconductors”, International Conference on Core Research and Engineering Science of Advanced Materials (Osaka, Japan, 30 May – 4 Jun., 2010).


6) T. Nozaki, “Voltage-induced magnetic anisotropy change in ultrathin Fe(Co)/MgO junctions”, 2011 MRS Spring Meeting and Exhibit (San Francisco, USA, Apr. 26, 2011).


MBE growth and magnetic properties of diluted magnetic semiconductors based on II-VI and IV-VI compounds

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Institute of Materials Science, University of Tsukuba

With an aim of searching for high-temperature ferromagnetism in semiconductors and of elucidating the mechanism of ferromagnetism, we have studied various materials of diluted magnetic semiconductors (DMSs) in which transition-metal (TM) elements are incorporated in II-VI or IV-VI compounds. We grew thin films of these DMSs by molecular beam epitaxy (MBE) and investigated structural and magnetic properties of the grown films. Our studies on the respective materials are described below.

1. Suppression of ferromagnetism due to co-doping of acceptor impurity in (Zn,Cr)Te

(Zn,Cr)Te has been regarded as a candidate of room-temperature ferromagnetic semiconductors[1]. It was also reported that the co-doping of donor or acceptor impurities in (Zn,Cr)Te has a significant effect on its magnetic properties; the ferromagnetism is enhanced by the co-doping of donor impurity iodine (I) [2] while it is suppressed by the co-doping of acceptor impurity nitrogen (N) [3]. In this study, we have investigated in a quantitative way how the magnetic properties and the electronic state of Cr change due to the N doping in order to clarify their correlation and to uncover to the origin of the suppression of ferromagnetism[4].

We prepared a series of N-doped Zn_{1-x}Cr_{x}Te thin films grown by MBE with a systematic variation of Cr composition in the range of Cr compositions of $x = 0.01 – 0.1$ and N concentration $[N]$ in the range of $10^{18} – 10^{20} \text{cm}^{-3}$. We measured the magnetization of the grown thin films under the application of magnetic field perpendicular to the film plane. We also performed X-ray absorption fine structure (XAFS) measurement at Cr K-edge to get the information of the electronic state of Cr.

The magnetization measurement reveals that the ferromagnetism disappears at the amount of $[N]$ corresponding to an almost constant ratio of $[N]/[Cr] = 0.08–0.1$. Figure 1 plots the three characteristic temperatures representing the critical behaviors of ferromagnetic transition as a function of $[N]$ for an almost fixed Cr composition in the range of $x = 0.06 ~ 0.09$. As shown in the figure, all these temperatures decrease gradually with $[N]$ at first, but suddenly drop to zero at $[N] = 1\times10^{20} \text{cm}^{-3}$, corresponding to the ratio $[N]/[Cr] \sim 0.08$. For the other values of Cr composition $x = 0.01$ and 0.03, the ferromagnetism disappears at the amount of $[N]$ corresponding to the ratio $[N]/[Cr] = 0.08 \sim 0.1$.

On the other hand, the X-ray near edge fine structure (XANES) at Cr K-edge exhibits an abrupt

![Figure 1: The three characteristic temperatures representing critical behaviors of magnetization, the Curie temperature $T_C$, the blocking temperature $T_B$, and the paramagnetic Curie-Weiss temperature $\Theta_p$, are plotted as a function of $[N]$ for an almost fixed Cr compositions $x = 0.06 \sim 0.09$. The scale of the ratio $[N]/[Cr]$ is also shown below.](image-url)
change in the features of the shoulder peak at the amount of [N] corresponding to the ratio [N]/[Cr] = 0.07 ~ 0.08. This correlation between the changes in magnetism and XANES suggests that the suppression of ferromagnetism can be attributed to the change of the Cr electronic state due to the acceptor doping.

2. MBE growth and magnetic properties of (Zn,Fe)Te thin films

DMs in which Fe is incorporated in II-VI compounds have been long studied and reported to exhibit van-Vleck type paramagnetism[5]. However, experimental studies on Fe-incorporated telluride was limited to those containing only a small Fe composition less than 1%[6]. In this study, we have attempted to grow thin films (Zn,Fe)Te with a higher Fe content by MBE and have investigated the structural and magnetic properties[7].

We prepared a series of Zn$_{1-x}$Fe$_x$Te thin films with Fe compositions of $x = 0 \sim 0.2$ grown by MBE in a systematic variation of the ratio between Zn and Te fluxes and the substrate temperature during the growth. We examined the crystal structure of the grown films by x-ray diffraction (XRD) and transmission electron microscope (TEM) and investigated the magnetic properties.

As a result, it is found that the structural and magnetic properties are different according as the films were grown either in the excess of Te flux (Te-rich) or in the excess of Zn flux (Zn-rich). In the XRD $\theta$-2$\theta$ scan, additional diffraction peaks assigned as FeTe of the tetragonal structure are detected in the films grown in the Te-rich condition, while no other peaks from extrinsic precipitates appear in the films grown in the Zn-rich condition. In the magnetization measurement, the films grown in the Te-rich condition exhibit paramagnetism up to $x \sim 0.08$ while those grown in the Zn-rich condition exhibit ferromagnetic behaviors such as hysteresis in the magnetization curve for $x > 0.03$. The ferromagnetic transition temperature $T_C$ deduced from Arrott plot analysis reaches 320K. The origin of the ferromagnetic behaviors observed in the films grown in the Zn-rich condition can be attributed to the formation extrinsic precipitates or Fe-aggregated regions which are structurally coherent to the host matrix.

3. Quaternary DMS compounds containing two kinds of transition metals

In the studies on DMSs so far, ternary compounds containing only one kind of magnetic element have mainly been investigated, while quaternary compounds containing two kinds of magnetic element have rarely been reported. In quaternary DMSs, however, a robust magnetic ordering might possibly be realized due to the interaction between different kinds of magnetic element. In particular, in a special combination of TM elements, such as Cr and Fe in II-VI compounds, it was theoretically predicted[8] that the two kinds of TM elements are coupled antiferromagnetically and a half-metallic electronic state is realized. In this study, we have investigated magnetic properties of a quaternary DMS in which Cr and Fe are incorporated in ZnTe.

We prepared a series of thin films of Zn$_{1-x-y}$Cr$_x$Fe$_y$Te with a fixed Cr composition $x \sim 0.06$ and

![Figure 2: The coercive force $H_C$ and saturation magnetization $M_s$ at 2K are plotted against Fe content $y$ for Zn$_{1-x-y}$Cr$_x$Fe$_y$Te thin films with a fixed Cr content $x \sim 0.06$.](image)
varied Fe composition \( y \) in the range of \( y = 0 \sim 0.02 \) grown by MBE. The magnetization measurement reveals that ferromagnetic behaviors observed in (Zn,Cr)Te is enhanced by the incorporation of Fe. Figure 2 plots the coercive course \( H_C \), the saturation magnetization \( M_S \) at 2K as a function of Fe composition \( y \) for the fixed Cr composition \( x = 0.06 \). With the increase of Fe composition, the coercive force \( H_C \) increases, while the saturation magnetization \( M_S \) decreases. These results are seemingly consistent with the theoretical prediction of antiferromagnetic coupling between Cr and Fe.

4. MBE growth and magnetic properties of (Sn,Mn)Te thin films

DMSs based on IV-VI compounds have been expected to exhibit ferromagnetism at a high temperature due to the carrier-induced mechanism[9,10]. Among various IV-VI compounds, SnTe has also been attracting attention as a typical material of topological crystalline insulator[11]. Then, it is interesting how the properties of topological surface state is changed by the incorporation of magnetic impurities, which are expected to break the time-reversal symmetry, requisite for the protection of the topological surface state. In this study, we have investigated the magnetic properties of (Sn,Mn)Te thin films grown by MBE. We grew thin films of (Sn,Mn)Te on a BaF\(_2\) (111) substrate using a compound source of SnTe and an elemental source of Mn. By optimizing the MBE growth conditions, we have succeeded to obtain Sn\(_{1-x}\)Mn\(_x\)Te epitaxial films grown only in the (111) orientation without a mixture with regions grown in other orientations up to a Mn composition around \( x = 0.06 \). In the magnetization measurement, only paramagnetic behaviors are observed in the magnetization curve down to 2K. The absence of ferromagnetic behaviors may be due to relatively low values of Mn composition and hole concentration in the grown films[12]. We are now attempting to achieve a higher Mn composition without a formation of extrinsic precipitates and a mixture with regions grown in other orientations.

References

List of publications
3) K. Zhang, R. Akiyama, K. Kanazawa, S. Kuroda, H. Ofuchi, “Effect of acceptor co-doping on magnetism and electronic states in ferromagnetic semiconductor (Zn,Cr)Te”, phys. stat. sol. (c)
5) (c) 7-8, 1320-1323 (2014).

List of invited talks
Surface plasmons and magneto-optics in metal/magnetic quantum wells

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1. Introduction

It has been known that optical and magnetic properties in oxide semiconductor materials have provided interesting physical aspects such as excitonic emissions, magnetic-optics and photo-catalysis. In this work, we focus on surface plasmons that have been applied for optical nanodevices. Surface plasmon resonances combined with light and magnetism are expected to be promising for new optical technology. Therefore, it is important to understand optical transitions in oxide semiconductors and their interactions with surface plasmons under light irradiations. Recently, surface plasmons excited on metallic surfaces have received much attention for investigations concerning optical functionalities on metal/semiconductor hybrid heterostructures. Strong electric fields induced around metallic surfaces play an important role for enhancements of optical excitations in semiconductor layers. Optical dynamics of energy transfer determine optical properties of semiconductors. In this study, we further develop optical interactions between magnetism and surface plasmons. Therefore, we will be required to understand light coupling of excitonic systems in semiconductors with surface plasmons.

2.1 Polarization filtering: theoretical and experimental approaches

High polarization filters in the UV range are expected to be promising for optical sensing and light detections. Nonpolar ZnO has self-polarization derived from asymmetric atom arrangement, which is much effective to produce polarization filter devices. Figure 1 shows energy levels and splitting of the valence band (V.B.) in nonpolar ZnO as a function of in-plane lattice strains ($\varepsilon_{yy}$ and $\varepsilon_{zz}$). These 2D results were calculated from the $k \cdot p$ theory perturbation.

![Fig. 1. In-plane lattice strains ($\varepsilon_{yy}$, $\varepsilon_{zz}$) and energy splitting $\Delta E_{31}$ (a) and $\Delta E_{32}$ (b) of the valence band (V.B.). (c) schematic picture of energy levels of V.B.](image-url)
The introduction of in-plane compressive strains into the ZnO layers provided high energy splitting based on energy transition related to the $E_1$ and $E_3$ in the V.B, leading to high polarization degree. Figure 2 shows polarization degree as a function of photon energy in the ZnO layers. The ZnO layer with in-plane compressive strains ($\varepsilon_{yy} = -0.1\%$, $\varepsilon_{zz} = -0.42\%$) exhibited high polarization degree of 19.8 as compared to ZnO layers ($\Phi = 8.2$) without in-plane compressive strain ($\varepsilon_{yy} = +0.42$, $\varepsilon_{zz} = -0.62\%$). The theoretical data were consistent with experimental results for realizing polarization filtering on ZnO.

### 2.2 Optical dynamics of metal/quantum well heterostructures

Dynamic processes of light energy transfer from metal to quantum wells are important to obtain performance of optical applications such as emitting devices and photo-catalysis. In this work, we employed a single quantum well (SQW) based on ZnO in order to monitor optical dynamics, and examined recombination lifetimes of excitons in a SQW by time-resolved photoluminescence. Optical interactions between lights and surface plasmons were studied.

A ZnO/Cd$_{0.08}$Zn$_{0.92}$O SQW with a 4.8 nm well width was grown by pulsed laser ablation (PLD). A well width ($L_W$) in the SQW was 4.8 nm. Ag nanoparticles (NPs) were also formed on the SQW by PLD. Figure 4 shows a cross-section TEM image of an Ag/ZnO SQW structure (Fig. 3a). Ag NPs arranged as a single monolayer, and exhibited plasmon resonances in the visible range at around 2.5 eV (Fig. 3b). Spatial separation between Ag NPs and SQW was about 5 nm (Fig. 3c). Excitonic PL from the SQW was similar to the plasmon peak of Ag NPs (Fig. 1d). Figure 4(a) shows temperature dependence of PL quenching in the Ag-coated SQW. The PL modulation was observed in low temperatures below 90 K (Fig. 4a). The PL intensity showed weak temperature dependence with an $S$ curve, indicating formations of localized excitons (Fig. 4b). Localization energy was 8.5 meV. Figure 5d shows TRPL decay curves of PL.
intensity in the un-coated SQW at 10 K, which could be fitted using two types of lifetimes (τ₁ and τ₂). τ₁ and τ₂ were 0.27 and 2.1 ns. In contrast, the Ag-coated SQW showed τ₁ = 0.24 and τ₂ = 1.7 ns. This demonstrated optical coupling between the plasmon energy of Ag NPs and excitons in the SQW. Their dynamics were cleared through this experiment.

2.3 surface plasmons and magneto-optic

Surface plasmons can be combined with magneto-optics (magnetic spins). For example, it has been known that Au/Co superlattices show large magneto-optical response, which are related to interactions between surface plasmons and magnetic properties. Therefore, it is expected to produce magneto-optical coupling between surface plasmons and magnetism.

We fabricated metal nanodot structures using top-down techniques, which showed plasmon resonances in the range from ultra-violet (UV) to visible (Fig. 5a). The plasmon resonance was dependent on nanodot size (volume). Furthermore, we evaluated degree of Zeeman splitting from Zn₀.₉₀Co₀.₁₀O layers with the metallic nanodots. Zeeman splitting only enhanced in low temperatures below 50 K (Fig. 5b), which showed the possibility of plasmon-induced magneto-optical enhancements in this research project. Hereafter, it will be required to understand optical coupling of surface plasmons with magneto-optics.

Fig. 4. (a) Temperature dependence of PL quenching. Inset indicates PL spectra of Ag-coated (red) and un-coated (black) SQWs. (b) Temperature dependence of PL peak energy from the SQW. (c) TRPL (lifetime) spectra of Ag-coated (red) and un-coated (black) SQW.

Fig. 5. (a) Surface plasmon spectra of Pd nanodot structures (dot diameter: 50 - 150 nm). (b) Zeeman splitting energy estimated from MCD spectra without (black) and with (red) metal nanodot.
3. **Summary**

In this work, we demonstrated optical interactions between surface plasmons, light and magnetism. In Se. 2.1, we presented high polarization filter devices based on ZnO from theoretical and experimental approaches. Furthermore, optical dynamics were investigated on the plasmon-exciton interactions of ZnO-based quantum wells combined with metallic nanostructures in SE. 2.2. Finally, we studied plasmon-induced magneto-optical modulation based on Zn$_{1-x}$Co$_x$O layers (Se. 2.3).

4. **Research representative**

Hiroaki Matsui (Assistant Professor, the University of Tokyo)

5. **Resultant outcomes**


Development of nonequilibrium dynamical mean-field theory and its application to low-dimensional strongly correlated systems

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Department of Physics, University of Tokyo

In this project, we have developed the nonequilibrium dynamical mean-field theory (DMFT), and applied the method to nonequilibrium phenomena in strongly correlated systems. In particular, we proposed to extend the nonequilibrium DMFT to cluster formalisms, which take account of non-local correlations in the time evolution of strongly correlated systems. The nonequilibrium dynamical cluster theory was applied to the Hubbard model, where we found a characteristic momentum-dependent relaxation dynamics. We have also studied nonequilibrium dynamics of electron-phonon systems and superconductors.

1 Development of nonequilibrium DMFT

The nonequilibrium DMFT is a self-consistent formalism of calculating time evolution of quantum many-body systems that maps the corresponding lattice model to an impurity model embedded in an effective dynamical mean field (Fig. 1). The advantage of this approach is that (i) it can treat the thermodynamic (infinite system-size) limit, (ii) the result becomes exact in the large dimensional limit of lattice models, and (iii) it can cover long-time evolution until the system thermalizes. Our group has contributed to the development of the nonequilibrium DMFT from the early stage, and implemented impurity solvers such as weak-coupling perturbation expansions [6]. Now the nonequilibrium DMFT has been established as a powerful method to analyze various types of models including symmetry-broken phases [8]. Summarizing recent progress, we wrote a review article on the nonequilibrium DMFT [5].

2 Cluster extensions of nonequilibrium DMFT

The limitation of the nonequilibrium DMFT lies in the local approximation of the self-energy, which becomes better as the spatial dimension increases. However, when one consider low-dimensional systems (e.g., $d \leq 2$), the effect of non-local spatial fluctuations becomes important.

To include those effects, we proposed a cluster extension of the nonequilibrium DMFT (namely, the nonequilibrium dynamical cluster theory) [4]. This maps a lattice model to a cluster model instead of a single-site impurity model, which is a nonequilibrium generalization of existing equilibrium dynamical...
cluster theories. There are mainly two types of mapping: the cellular dynamical mean-field theory (CDMFT, real-space based) and dynamical cluster approximation (DCA, momentum-space based). We adopted the latter (Fig. 2) since it keeps the lattice translational symmetry.

We applied the nonequilibrium DCA to the interaction quench problem for the one- and two-dimensional Hubbard models. As a simple cluster solver, we used the iterative perturbation theory. In 1D, we benchmarked the method by comparing the results with the time-dependent density matrix renormalization group. It turned out that results for local or nearly local quantities (that can be defined within the cluster) converge very rapidly with respect to the cluster size $N_c$. On the other hand, the results are greatly improved from those of the nonequilibrium DMFT (i.e., $N_c = 1$ case), which predicts too fast thermalization. This means that non-local correlation effects are quite important even for (nearly) local quantities.

In 2D, local quantities calculated by the nonequilibrium DCA agree well with those obtained from the nonequilibrium DMFT, and $N_c$ dependence is relatively weak compared to the 1D case. The non-local effects become critical when highly non-local quantities such as the momentum distribution are concerned. While the nonequilibrium DMFT always gives a momentum-independent relaxation, the nonequilibrium DCA shows that the system relaxes quite inhomogeneously in momentum space: the momentum distribution at the Fermi surface relaxes to the thermal one faster near $k = (\pm \pi, 0)$, $(0, \pm \pi)$ than near $k = (\pm \pi/2, \pm \pi/2)$. This can be explained by the momentum-dependent lifetime of quasiparticles $\tau(k)^{-1} \propto \text{Im}\Sigma_R^R(k, \omega)$. In fact, it agrees with the relaxation time extracted from the nonequilibrium DCA results. In the present case, the 2D Hubbard model at half filling has a van Hove singularity, due to which the system behaves as a marginal Fermi liquid (Im$\Sigma_R^R(k, \omega) \propto \omega$ around $\omega = \varepsilon_F$).

3 Applications to electron-phonon systems

The role of the electron-phonon interaction for nonequilibrium dynamics of superconductors has not been fully understood yet. We focused on the (Hubbard-)Holstein model, one of the representative models of electron-phonon systems, and studied its equilibrium ordered phases using DMFT [2][7]. As an impurity solver, we extended the continuous-time quantum Monte Carlo method to be able to treat ordered phases, including superconductivity, antiferromagnetism, and charge density wave, on an equal footing.

The DMFT calculation showed that the Holstein model on a bipartite lattice exhibited the supersolid phase (i.e., coexistence of superconductivity and charge density wave) at the intermediate electron-phonon
coupling regime [2]. The supersolid phase is different from a hysteretic region near first order phase transition, and is stable against phase separation. Accompanied by the emergence of the supersolid phase, a quantum critical point (QCP) appears between the superconducting and supersolid phases. At the QCP, charge fluctuation diverges, and the superfluid density (or London penetration depth) shows kink-like singular dependence on the filling. We further studied various aspects of the newly found supersolid phase of the Holstein model.

We also investigated the dynamics and relaxation process of the Holstein model using the nonequilibrium DMFT with the self-consistent Migdal approximation as an impurity solver [1]. It was revealed that the dominant thermalization process crossovers from electron to phonon degrees of freedom as one increases the electron-phonon coupling strength. On the weaker coupling side, the coherent phonon oscillation decays faster than the relaxation of the electron momentum distribution. On the stronger coupling side, the phonon oscillation is long-lived, and the electron momentum distribution effectively thermalizes at each time with the nonequilibrium phonon background. This kind of “two-step relaxations” (i.e., electrons relax faster and phonons relax later) occurs even without an electron-electron interaction on top of the electron-phonon interaction.

4 Applications to superconducting systems

We extended the nonequilibrium DMFT to the superconducting phase, and applied it to the quench problem for the attractive Hubbard model (the same results are equally applied to the antiferromagnetic phase of the repulsive Hubbard model due to the duality between the repulsive and attractive models at half filling) [8]. It was found that the system is trapped to a nonthermal quasi-stationary state for a while after excitation. This quasi-stationary state (called the nonthermal fixed point) maintains a long-range superconducting order up to certain time scale even when the excitation energy, if transformed to heat, amounts to temperature higher than the thermal critical temperature. As one varies the excitation energy, the stationary state vanishes, and the system starts to directly approach the thermal state. At this transition point (which is different from the thermal critical point), the relaxation time to the nonthermal fixed point diverges, and a characteristic critical behavior is observed.

The method was further applied to the superconducting phase of the attractive Hubbard model driven by a continuous ac electric field. The results indicated that the ac driving field with frequency $\Omega$ generates a coherent oscillation of the superconducting order parameter with frequency $2\Omega$. This is due to the nonlinear coupling ($A^2\Psi$) between the amplitude of the order parameter $\Psi$ and the electric field $A$. Moreover, the amplitude of this $2\Omega$ oscillation of the order parameter is maximized when $2\Omega$ coincides with the superconducting gap $2\Delta$. This was explained by the resonance between the external driving and the Higgs amplitude mode inherent in superconductors whose eigenfrequency in the weak-coupling regime is $2\Delta$. This so-called Higgs-mode resonance phenomenon was recently observed in a terahertz laser experiment using a conventional low-temperature superconductor [3].

5 Cooperation researchers, Collaborators

Cooperation researchers:

- Hideo Aoki (Department of Physics, University of Tokyo)
- Takashi Oka (Department of Applied Physics, University of Tokyo)

Collaborators:

- Philipp Werner (University of Fribourg)
- Martin Eckstein (University of Hamburg)
- Peter Barmettler (University of Geneva)
• Yuta Murakami (University of Tokyo)

6 Invited talks (12 talks in total)

(1) N. Tsuji, "Higgs mode in conventional and unconventional superconductors", A workshop on "Nonequilibrium phase transitions in diverse physical systems" (9 December 2014, Tokyo, Japan).


(3) N. Tsuji, "Higgs mode and Anderson pseudospin resonance in superconductors", Higgs modes in condensed matter and quantum gases (24 June 2014, Kyoto, Japan).


(5) N. Tsuji, "Nonthermal fixed point in the antiferromagnetic Hubbard model", Non-equilibrium dynamics of correlated electron-systems (19 December 2013, Krvavec, Slovenia).

(6) N. Tsuji, "Prethermalization and nonthermal fixed point in the Hubbard model", Interdisciplinary mini-workshop on nonequilibrium physics (8 December 2013, Kyoto, Japan).

7 Published papers (11 papers in total)


Effect of electron-phonon couplings on electronic structures and material design

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1. Introduction

In recent years, first-principles calculations based on the density functional theory (DFT) have become essential tools to investigate the electronic structures of various materials. Moreover, advanced methods to discuss corrections for the DFT results such as GW approximation has been developed intensively. In this study, we focus on another correction for the DFT results, that is, the effect of electron-phonon couplings. First, we have developed two different codes based on the frozen phonon method and the density functional perturbation theory (DFPT) and confirmed that these two approaches give consistent results and well reproduce experiments. By employing these methods, we have discussed the temperature and isotope dependence of band structures, and possibility of material design by utilizing the electron-phonon couplings and isotope effects. We believe our study is of great importance for the understandings of the effect of electron-phonon couplings from first-principles calculations.

2. Results

1) Isotope effect on the band structure of diamond and graphene

It has been known that the band gap of diamond is reduced due to electron-phonon couplings even at T=0 and the reduction has large temperature dependence. This means that the band gap also has isotope dependence. Even a superlattice structure made of \(^{12}\text{C}\) and \(^{13}\text{C}\) has been synthesized to utilize the isotope effect. To discuss electronic structures in such nanostructures made of \(^{12}\text{C}\) and \(^{13}\text{C}\), it is of great importance to discuss the difference of the band gap, band offset and so on in \(^{12}\text{C}\) diamond and \(^{13}\text{C}\) diamond. For this end, we have synthesized highly pure impurity-free diamond using chemical vapor deposition (CVD) method for several isotope compositions and have discussed the isotope dependence of the band gap experimentally and theoretically.

First, we determined the isotope composition in obtained CVD diamond by Raman peak positions. From the width of the Raman peak, we also found that the obtained diamond is quite clean and impurity and defect free. Figure 1 shows the Cathode luminescence (CL) spectra of diamond with the isotope composition of \(^{12}\text{C}_{1-x}^{13}\text{C}_x\). As can be seen, the peak positions have large isotope dependence. These peaks correspond to the indirect band gap of diamond. Thus, considering the isotope dependence of the phonon mode with including the randomness, we obtained the following expression for the band gap:
Here, \( x_f \) is the ratio of \(^{13}\text{C}\) in diamond. This indicates that the difference of the band gap between \(^{12}\text{C}\) and \(^{13}\text{C}\) diamond is 15.4 meV [11].

On the other hand, we also estimated theoretically the isotope effect by calculating the second order terms of electron-phonon couplings, that is, self-energy term and Debye-Waller term within the density functional perturbation theory. Figure 2 shows the temperature dependence of the indirect band gap in \(^{12}\text{C}\) diamond due to these two terms together with the thermal expansion effect, which comes from higher order terms in electron-phonon couplings. This temperature dependence well agrees with the experiments. Using this result, we can estimate that the difference of band gap between \(^{12}\text{C}\) and \(^{13}\text{C}\) diamond is 12 meV at \( T=0 \). Furthermore, the band offsets at the conduction bottom and the valence top are found to be about 7 meV and 5 meV respectively.

In case of graphene, using the same method, we found that the work function becomes different in \(^{12}\text{C}\) and \(^{13}\text{C}\) due to electron-phonon couplings. This suggests that the junction of \(^{12}\text{C}\) and \(^{13}\text{C}\) graphene would be a pn-junction without applying a gate voltage. We also discussed the possibility of band gap opening using the periodic patterning of carbon isotope.

2) Phonon properties in an adamantane monolayer on a Au(111) surface

Adamantane is the smallest diamondoid, which can be regarded as small pieces of hydrogen-terminated diamond as shown in Fig. 3 and is known to exhibit negative electron affinity. Using this molecule, we discussed how the vibrational...
properties of a monolayer of the molecule are affected by a surface. For this purpose, we performed first-principles calculations and compared the results with the newly developed infrared scanning tunneling microscopy (IRSTM) technique. The results indicate that the IR spectrum is significantly modified due to both intermolecular and molecule-substrate interaction. The theoretical calculations agree well with IRSTM experiments, suggesting that these techniques are useful to discuss the properties of few-layer materials on substrate[10].

3) Evaluation of model parameters in κ-(ET)$_2$X

To design a superconducting material, organic compounds are one of the most promising materials. For example, A15 Cs$_3$C$_{60}$ has high transition temperature of T$_c$=38K, which is one of the highest T$_c$ within phonon-mediated superconductors. On the other hand, organic conductors such as κ-(ET)$_2$X also host superconductivity. However, these materials are close to the Mott insulator in the phase space, and thus, the Coulomb interaction is considered to be important for superconductivity. In other words, even though both systems can be regarded as carrier doped organic compounds, completely different mechanisms are considered to be important for superconductivity. To clarify the difference of these organic compounds, systematic approaches from the first-principles calculations are of great importance. For this end, we first obtained the electronic structures of several κ-(ET)$_2$X and constructed tight-binding models.

Figure 4 shows the obtained DFT band structures and tight-binding fits. Analyzing the obtained tight-binding model, we concluded that the material dependences in κ-ET compounds come mainly from anisotropy of the transfer integrals in anisotropic triangular lattice model rather than the on-site (on-dimer) Coulomb interaction[7]. Based on this study, we will discuss the intra-dimer degrees of freedom, the phonon properties and superconductivity in these compounds.

4) Large surface relaxation in the organic semiconductor tetracene

In organic crystals, inter-molecular interactions play an important role in determining their structures as well as their phonon properties. In particular, the surface relaxation is a key issue for the design of organic nanodevices. Thus, we studied surface relaxation in semiconductor tetracene theoretically and experimentally. Using X-ray crystal truncation rod scattering measurements, a significant surface relaxation was observed only in the first monolayer. This strong relaxation can be reproduced by the first-principles calculations. We also found that the
transfer integrals and as a result transport properties are completely different between the bulk and surface of the semiconductor[4].

3. References


4. Invited talks

4 invited talks in the international conferences and 7 in domestic conferences.
Development of Computational Code of Electron Excitation Dynamics in Green’s Function Method

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1. INTRODUCTION

The Green's function method in the many-body perturbation theory plays a powerful role in first-principles calculations of excited states of materials. Almost 50 years ago, Hedin proposed a closed set of equations for Green's function, the dynamically screened Coulomb interaction \( W \) (composed of the polarization function \( P \)), and the vertex function \( \Gamma \). Its simplest approximation is called the GW approximation or the self-consistent GW approach, where the vertex function is replaced by unity. In this approximation, \( P \) and \( W \) become those of the random phase approximation (RPA) and the self-energy \( \Sigma \) is given by \( iGW \) symbolically.

However, as a deficiency of the self-consistent GW approximation, the Ward-Takahashi identity, which is derived from gauge invariance, is not satisfied. Consequently, the band gap is overestimated. In order to satisfy the Ward-Takahashi identity, the vertex function must be included in the self-energy and the polarization function, which is a very difficult task.

Another difficulty in the quasiparticle representation is that the quasiparticle wavefunctions are non-orthonormal and linearly dependent due to the energy dependence of the self-energy. One way to solve this problem is to use Löwdin's symmetrized orthonormalization procedure, but there is a big question how to deal with this energy dependence when the quasiparticle equation is solved self-consistently.

Here, we propose a simple and practical way to solve these problems. Our idea is to linearize the energy dependence of the self-energy. The key point in the present formulation is to guarantee its relation to the Ward identity, i.e., the \( q = 0 \) and \( \omega - \omega' = 0 \) limit of Ward-Takahashi identity. As a result, the quasiparticle energies are greatly improved for Li and Na (atoms and dimers). Within this approach, we also calculate the total energy for the ground state. Since the direct calculation of the Luttinger-Ward functional \( \Phi \) is a heavy task, we propose more convenient formulae on the basis of a plasmon-pole model. Here we use the all-electron mixed basis approach (the name of our program is TOMBO), in which quasiparticle wavefunctions are expanded with atomic orbitals and plane waves.

On the other hand, it has been highly desired to go beyond the time-dependent density functional theory (TDDFT) within the local (time and space) density approximation in the investigation of time-dependent correlated electron systems, because there is a delay in electron dynamics, and correlation between two electrons or two holes cannot be treated in this framework. One possibility to go beyond the TDDFT is to invoke the time-dependent Green’s function formalism in the quantum many-body perturbation theory. We have formulated such a theory, and now implementing it into TOMBO.
2. THEORY

The quasiparticle equation can be written as

\[
(T + v_{\text{nuc}} + \Sigma(\epsilon_n)) | n > = \epsilon_n | n > ,
\]

(1)

where the eigenstates \( | n > \) are the quasiparticle states, the eigenvalues \( \epsilon_n \) are the quasiparticle energies, \( T \) is the kinetic energy operator, \( v_{\text{nuc}} \) is the nucleus Coulomb potential, and \( \Sigma(\epsilon_n) \) is the self-energy operator. Note that the self-energy operator is energy dependent, and therefore the quasiparticle states are non-orthonormal and linearly dependent. This fact makes the subsequent formulation very difficult. To avoid this difficulty, we expand the self-energy with respect to the eigenvalue \( \epsilon_n \) to obtain

\[
H | n > = \epsilon_n | n > ,
\]

\[
H = T + v_{\text{nuc}} + \Sigma(\mu) - \mu \frac{d\Sigma(\omega)}{d\omega} | \omega = \mu ,
\]

(2)

where \( \Lambda \) is defined by

\[
\Lambda = 1 - \frac{d\Sigma(\omega)}{d\omega} | \omega = \mu .
\]

(3)

Here, \( \mu \) can be set, for example, at the mean eigenvalue of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels. Here we use \( n \)-independent \( \mu \) and \( \Lambda \), and the Cholesky decomposition with the lower triangular matrix \( L \) as

\[
\Lambda = LL^\dagger
\]

(4)

Then we can naturally define the orthonormalized quasiparticle states and the corresponding Hamiltonian as

\[
\tilde{n} > = L^\dagger | n > , \quad \tilde{\mathcal{O}} = LL^{-1} H L^{-1}\dagger.
\]

(5)

As a consequence, we have the linearized quasiparticle equation:

\[
\tilde{\mathcal{O}} | \tilde{n} > = \epsilon_n | \tilde{n} >
\]

(6)

The orthonormalized states satisfy the following orthonormality and completeness conditions:

\[
< \tilde{n} | \tilde{a} > = \delta_{na}, \quad \Sigma_n | \tilde{n} > < \tilde{n} | = 1 .
\]

(7)

The occupation number of these states is purely zero or one according to whether the corresponding quasiparticle energy is above or below the Fermi level. In contrast, the original quasiparticle states satisfy \( < n | A | a > = \delta_{na} \) and \( \Sigma_n | n > < n | = \Lambda^{-1} \). Since \( | n > \) do not satisfy the completeness condition, Green's function defined in this linearized framework,

\[
G(\omega) = \Sigma_n | n > 1/(\omega - \epsilon_n - i\eta_n) < n | = \Sigma_n \Lambda / [(\omega - i\eta_n)A - H] | n > < n |,
\]

(8)

(\( \epsilon_n \) is 0\(^\dagger \) for occupied states \( n \) and 0\(^\circ \) for empty states \( n \).) does not have a `resolvent" form. This Green's function does not satisfy the charge conservation law. In fact, it is easy to see that

\[
-\frac{i}{\hbar} \int dr \int d\omega 2\pi \exp(i\eta \omega) < r | G(\omega) | r > \neq N , \quad \text{where} \ \eta \ \text{is a positive infinitesimal number (0\(^\circ \)).}
\]

This violation of the charge conservation is related to the existence of the incoherent part in Green's function. In order to avoid this difficulty, we introduce the renormalized Green's function as:
The original Green's function is given by
$$\tilde{A}(\omega) = L^+ G(\omega) L = \sum_n | \tilde{n} > 1 / (\omega - \varepsilon_n - i\eta_n) < \tilde{n} | = \sum_n | \tilde{n} > < \tilde{n} | 1 / (\omega - i\eta_n - \tilde{\Omega}).$$  (9)

In this representation, since the quasiparticle states are orthonormal, Eq.(9) with tilde $G(w)$ in place of $G$ satisfies the charge conservation,
$$\oint \rho(r) \, dr = -i \oint dr \int d\omega/2\pi \exp(i\omega \cdot r) < r | \tilde{A}(\omega) | r > = N,$$  (10)
and the electron charge density $\rho(r)$ is given by
$$\rho(r) = \sum_n \text{occ} \ | < r | \tilde{n} > |^2,$$  (11)
where occ means to take the summation over all occupied states. Note that the coherent part of the polarization function is given by $G(\omega) = L^{+\dagger} \tilde{A}(\omega) L^\dagger$, and the matrices $L^{+\dagger}$ and $L^\dagger$ correspond to the square root of the renormalization factor $Z = \Lambda^{-1}$. Then we should write the Hartree term as
$$\Sigma_0 \rho(r) = -i \int dr' \nu(r-r') \int d\omega/2\pi \exp(i\eta \omega) \tilde{A}(r, r'; \omega) = \int dr' \nu(r-r') \rho(r'),$$  (12)
where $\nu(r-r')$ is the bare Coulomb interaction.

The most important fact here is that the vertex function is related to $\Lambda$ via the Ward identity, i.e., the Ward-Takahashi identity in the $q=0$ and $\omega - \omega' = 0$ limit,
$$\Pi(\omega = \mu, \omega' = \mu; q = 0) = 1 - d\Sigma/\omega|_{\omega=0} = \Lambda.$$  (13)

This relation can be also written as the well-known formula $IZ = 1$. The formulation up to here is very general and can be applied to any Green's function-based framework. Then, according to the Hedin's set of equations, the self-energy $\Sigma_{xc}(\omega)$ except for the Hartree term is approximated as $i\tilde{A}W$, the dynamically screened Coulomb interaction $W$ is described by the polarization function $P$ and the interaction kernel $d\Sigma/dG$ as $W = [1 - i (d\Sigma/dG)P]^{-1}$. Since the exact polarization function $P$ is given by $P = -iGGF$ and the interaction kernel is given by $-iv\Lambda$, we find that $W$ is equal to $W = [1 - v\Pi]^{-1}$, where we defined the renormalized polarization function $\Pi$ as $\Pi = \Lambda P = -iAGG\Lambda - iAGA = -i\tilde{A}$. Therefore $\Sigma_{xc}(\omega)$ and $W$ are functionals only of $\tilde{A}$. Thus, our formulation is identical to that of the non-linearized self-consistent GW approach with $G$ replaced by $\tilde{A}$. (Ref.: PUBLICATION No.5.)

3. RESULTS

Table 1. IP and EA of LGW and other results of Li, Na atoms and dimers compared with the preexisting experimental data. (Ref.: PUBLICATION No.5.)

<table>
<thead>
<tr>
<th>(eV)</th>
<th>Li</th>
<th>Li2</th>
<th>Na</th>
<th>Na2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IP</td>
<td>EA</td>
<td>IP</td>
<td>EA</td>
</tr>
<tr>
<td>LDA</td>
<td>3.14</td>
<td>1.83</td>
<td>3.24</td>
<td>1.84</td>
</tr>
<tr>
<td>HF</td>
<td>5.34</td>
<td>0.04</td>
<td>4.88</td>
<td>0.08</td>
</tr>
<tr>
<td>B3LYP</td>
<td>3.34</td>
<td>1.00</td>
<td>3.30</td>
<td>0.99</td>
</tr>
<tr>
<td>GW</td>
<td>5.78</td>
<td>0.22</td>
<td>5.56</td>
<td>0.20</td>
</tr>
<tr>
<td>LGW</td>
<td>5.66</td>
<td>0.28</td>
<td>5.32</td>
<td>0.35</td>
</tr>
<tr>
<td>Previous GW</td>
<td>--</td>
<td>--</td>
<td>4.6</td>
<td>--</td>
</tr>
<tr>
<td>Experiment</td>
<td>5.39</td>
<td>0.62</td>
<td>5.15</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Using this linearized self-consistent GW (LGW) approach implemented in TOMBO, we have calculated the ionization potential (IP) and the electron affinity (EA) of Li, Li$_2$, Na, and Na$_2$. Table 1 shows the result together with the results obtained by other methods (LDA, HF, and B3LYP) as well as the preexisting experimental data. Because the LGW values are the closest to the experimental values except for the HF, IP of Li, we find that the LGW significantly improves the results of the ordinary self-consistent GW result and other results. (Ref.: PUBLICATION No.5.)

4. SUMMARY

We have formulated the linearized self-consistent GW approach, implemented it into the all-electron mixed basis program, TOMBO, and found that the resulting quasiparticle energies are greatly improved compared to the ordinary self-consistent GW and other approaches such as LDA, HF, B3LYP. Although we did not show explicitly here, we have also proposed the convenient formula to evaluate the Luttinger-Ward functional $\Phi$ using a plasmon pole model and calculated the total energy of Li and Na (atoms and dimers).

Furthermore, we have succeeded in formulating the time-dependent Green’s function theory for the excited state by extending the ordinary Green’s function theory for the ground state. We are now implementing it into TOMBO and submitting a paper.

5. PUBLICATIONS


Large Scale First-Principles Calculations on Transition Metal Oxide Superlattices

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1. Introduction

Recently, the two-dimensional electron gas (2DEG) formed at the transition metal oxides interface has attracted much attention for applications in the next generation device. The perovskite heterostructure composed dielectric materials LaAlO$_3$/SrTiO$_3$ is one of such systems extensively studied. The polar interface induces large built-in electric field. Therefore, the electric-field induced spin-orbit interaction (SOI) in the perovskite heterostructure is quite important in understanding the electronic structures.

In this research, by using large-scale first-principles calculations based on the density functional theory implemented OpenMX[1], we revealed specific electronic states and properties formed at the interface of the transition metal oxides modeled by superlattice. We focused on how spins can be controlled by electric field (electric polarizations and charge carriers). In additions to the 2DEG in the oxides heterostructure, we also revealed that the effect of SOI in strained ZnO bulk and film, the spin textures at the surface of topological insulators, carrier-induced magnetism in bilayer zigzag-edged graphene nanoribbons, and triangular lattice multiferroic oxides. The applications of 2DEG at the oxide interface, we proposed anomalous Seebeck effect.

2. Rashba effect in the (LaAlO$_3$)$_n$/SrTiO$_3$$_n$ superlattice

We have performed first-principles calculations of (LaAlO$_3$)$_n$/SrTiO$_3$$_n$ (n=2-8). We evaluated the spin-orbit coupling constant, the Rashba parameter, for the interface states. In addition, we investigated the spin textures, i.e., momentum vector dependent magnetic field

---

Figure 1 (a) Structure of (LaAlO$_3$)$_6$/SrTiO$_3$$_6$ and (b) atom projected density of states. The numbers in parenthesis is layer index. The dotted line in the density of states show the bottom of the Ti 3d states in the conduction bands.
$B(k)$ in the Brillouin zone. Figure 1(a) shows artificial superlattice \((\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6\). As we assumed SrTiO$_3$ substrate, the in-plane lattice constants are SrTiO$_3$ as 0.395 nm. Lattice constant $c$, the period of superlattice, is determined by constant volume approximation where the volume is equivalent to bulk. Figure 1(b) shows atom projected density of states. We can evaluated built-in electric field by energy level at the bottom of the empty Ti 3$d$ states. The estimated value of electric field 768 meV/nm is in good agreement with experimental value 801 meV/nm[2]. Figure 2 shows atomic displacement relative to ideal structure, i.e., bulk-like locally non-polar structures. If we assumed point charge ionic model as Sr$^{2+}$, La$^{3+}$, Al$^{3+}$, Ti$^{4+}$, and O$^{2-}$, the electric field can be understood by the atomic displacement. The direction of electric field is reflected in the spin textures of interface states as in figure 3 (a) and (b).

Spin-orbit effect in the ZnO

We have perform first-principle calculations of wurtzite ZnO bulk and thin-film (1010) surface system based on the density-functional theory (DFT) within the generalized gradient approximation by using the OpenMX code [1]. For the film case, we have performed large scale computation up to 120 ZnO bilayer and the period of unit cell is about 20 nm. We evaluated the spin texture whose energy is slightly higher than that of the conduction band bottom in bulk and surface bands in (1010) surface. We find that the Rashba spin rotations can be inversed by applying biaxial strain. This inversion of the rotation is due to the fact that the biaxial strain inverse the directions of the electronic polarization around the Zn atom. These findings suggest that the Rashba effect can be controlled by substrates. In the (1010) film case, we find that in-plane electric polarization induces the quasi-one dimensional orientations of the spin textures. Figure 4 shows calculated band structure of

Figure 2 Atomic displacement relative to ideal structure in \((\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6\).

Figure 3 Spin textures of interface states for \((\text{LaAlO}_3)_6/(\text{SrTiO}_3)_6\), (a) lower energy band, (b) higher energy band. The background is band energy and white color is Fermi energy.

Figure 4 Calculated band structure of ZnO (1010) ideal structure(purple line), relaxed structure (blue line) and bulk (gray line).
relaxed film and unrelaxed film, and bulk. We find surface states above bulk valence band top. The atomic relaxation drastically changes surface states. The atomic relaxation also changes the electric field at the surface. Therefore the spin textures and spin-orbit coupling constant of the surface states is strongly affected by the atomic relaxations. We find that the values of the spin-orbit strength and the wavelength of the spin-helix are comparable with those observed for various zinc-blende quantum well structures.

4. References

5. Publications and Invited Talks
Publications

Invited talks
Development of quantum multi-component molecular theory and its application to material design

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1. Introduction

Recently, in our group, we have developed and improved some first-principles approaches for quantum multi-component systems including both electrons and nuclei (sometimes positron, or muon) quantum-mechanically: Multi-component molecular orbital (MC_MO) [1], density functional theory (MC_DFT) [2], quantum Monte Carlo (MC_QMC) [3], and ab initio path integral (PI) [4] methods. In this KAKENHI research project, we have focused on the development of these quantum multi-component molecular theories and its microscopic (molecular level) application to material design as follows,

- Nuclear quantum effect and temperature dependency on the hydrogen-bonded structure of base pairs: path integral hybrid Monte Carlo approach with semi-empirical method
- Systematic theoretical investigation of a positron binding to amino acid molecules: ab initio multi-component molecular orbital approach
- Accurate prediction of hyperfine coupling constants in muoniated and hydrogenated ethyl radicals: ab initio path integral approach with density functional theory method
- Can formaldehyde molecule bind a positron? Theoretical prediction with state-of-the-art first principles calculation: multi component quantum Monte Carlo approach

Here, we would like to show main results, one by one.

2. Main results of our research project
2.1. Nuclear quantum effect and temperature dependency on the hydrogen-bonded structure of base pairs

The structure of Watson-Crick type Adenine-Thymine and Guanine-Cytosine pairs (Figure 1) has been studied by hybrid Monte Carlo (HMC) and path integral hybrid Monte Carlo (PIHMC) simulations (Figure 2) with the use of semi-empirical PM6-DH+ method in the gas phase. We elucidated the nuclear quantum effect and temperature dependency on the hydrogen-bonded moiety of base pairs. It was shown that the contribution of nuclear quantum effect on the hydrogen-bonded structure is significant not only at low temperature 150 K but also at temperature as high as 450K. The relative position of hydrogen-bonded proton between two heavy atoms, and the nuclear quantum nature of the proton are also shown (Figure 3).
Furthermore, we have applied principal component analysis to HMC and PIHMC simulations in order to analyze the nuclear quantum effect on intermolecular motions. We found that the ratio of Buckle mode (lowest vibrational mode from normal mode analysis) decreases due to the nuclear quantum effect, while that of Propeller mode (second lowest vibrational mode) increases. In addition, non-planar structure of base pairs was found to become stable due to the nuclear quantum effect from two-dimensional free energy landscape along Buckle and Propeller modes.

**Figure 2. Schematic illustration of path integral scheme for H$_2$ molecule**

![H$_2$ molecule with 8 beads](image)

**Figure 3. One-dimensional distributions of (a) $R_{N1H1}$ and (b) $R_{N1...O1}$**

2.2. Systematic theoretical investigation of a positron binding to amino acid molecules with ab initio multi-component molecular orbital approach

The feature of positron binding to twenty neutral amino acid molecules having the global minimum (GM) and the intramolecular hydrogen-bonded (HB) structures was analyzed with ab initio multi-component molecular orbital method. All amino acid molecules in the intramolecular HB structures have positive positron affinity (PA, the binding energy of a positron) values, which means that a positron can be attached to parent molecules, while in the GM structures only three amino acid molecules of Gln, Trp, and His have positive PA values. Analyzing the positronic orbitals of each positronic amino acid molecule and the electrostatic potential maps of the corresponding parent molecules, we found that the long-range electrostatic interaction is the most crucial role in the positron binding to neutral amino acid molecules (Figure 4). The strong correlation is observed between the PA and dipole moment, that is, a polar molecule with a large dipole moment has a large PA value (Figure 5). The critical dipole moment of neutral amino acid molecules for binding a positron is found as about 3.46 Debye. From the systematic analysis for twenty kinds of amino acid molecule, we theoretically confirmed the possibility of positron binding to conformers of amino acid molecules having strong dipole moment.
Figure 4. (a) The positronic molecular orbital and the electronic highest occupied molecular orbital (HOMO) of [Gly; e⁺] system in the hydrogen-bonded (HB) structure with Hartree-Fock (HF) level of the multi-component molecular orbital (MC-MO) method. Contours of isovalue 0.01 are drawn. The meshed region denotes the contour of the positronic orbital, while the red and green regions are of the positive and negative parts of the electronic HOMO, respectively. (b) The electrostatic potential (ESP) map of Gly in the HB structure. The intensity of ESP is coloured on electronic charge density surface with contours of isovalue 0.0004. The charges on nitrogen and oxygen atoms (δ) obtained with natural bond orbital (NBO) analyses are also shown.

Figure 5. The correlation between dipole moment values (Debye) and positron affinity values (meV) of amino acid molecules. The solid circles and squares denote the hydrogen-bonded (HB) and global minimum (GM) structures, respectively. The correlation coefficient ($R^2$) in linear regression analysis is also shown.
2.3. Accurate prediction of hyperfine coupling constants in muoniated and hydrogenated ethyl radicals: ab initio path integral simulation study with density functional theory method

We performed *ab initio* path integral molecular dynamics (PIMD) simulation (Figure 1) with density functional theory (DFT) method to accurately predict hyperfine coupling constants (HFCCs) in ethyl radical \((C_βH_3—C_αH_2)\) and its Mu-substituted (muoniated) compound \((C_βH_2Mu—C_αH_2)\) (Figure 6). The substitution of Mu atom, an ultra-light isotope of the H atom, with larger nuclear quantum effect is expected to strongly affect the nature of ethyl radical. The static conventional DFT calculations of \(C_βH_3—C_αH_2\) find that the elongation of one \(C_β—H\) bond causes a change in the shape of potential energy curve along the rotational angle via the imbalance of attractive and repulsive interactions between the methyl and methylene groups. Investigation of the methyl-group behavior including the nuclear quantum and thermal effects shows that unbalanced \(C_βH_2Mu\) group with the elongated \(C_β—Mu\) bond rotates around the \(C_β—C_α\) bond in muoniated ethyl radical, quite differently from the \(C_βH_3\) group with the three equivalent \(C_β—H\) bonds in ethyl radical. These rotations couple with other molecular motions such as the methylene-group rocking motion (inversion), leading to difficulties in reproducing the corresponding barrier heights. Our PIMD simulations successfully predict the barrier heights to be close to the experimental values, and provide a significant improvement in muon and proton HFCCs given by static conventional DFT method. Further investigation reveals that the \(C_β—Mu/H\) stretching motion, methyl-group rotation, methylene-group rocking motion, and HFCC values deeply intertwine with each other. Because these motions are different between the radicals, a proper description of the structural fluctuations reflecting the nuclear quantum and thermal effects is vital to evaluate HFCC values in theory to be comparable to the experimental ones (Table 1). Accordingly, a fundamental difference in HFCC between the radicals arises from their intrinsic molecular motions at a finite temperature, in particular the methyl-group behavior.

![Figure 6. Schematic illustration of muonated ethyl radical.](image)

**Table 1. Bond lengths and HFCC values.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Conventional MO</th>
<th>PIMD</th>
<th>Exptl.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mu</td>
<td>H</td>
<td>Mu</td>
</tr>
<tr>
<td>Bond Length [Å]</td>
<td>1.104</td>
<td>1.17</td>
<td>1.12</td>
</tr>
<tr>
<td>(R(C_β—X))</td>
<td>5.36</td>
<td>4.2</td>
<td>3.70</td>
</tr>
<tr>
<td>Isotropic HFCC [mT]</td>
<td>2.67</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>(A'(Mu))</td>
<td>Reduced Mu HFCC: (A'(Mu) = 0.31413 \times A(Mu))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A(Me))</td>
<td>Averaged HFCC for (CH_2Mu) or (CH_3) group</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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2.4. Can formaldehyde molecule bind a positron?
Theoretical prediction with state-of-the-art first principles calculation

The vertical positron affinity (PA) value at the equilibrium position of formaldehyde molecule is predicted as +25(3) meV with highly accurate quantum Monte Carlo method. Applying the anharmonic vibrational analysis, we have found that the vibrational excitation of C=O stretching mode drastically enhances the PA value, due to the increment of molecular dipole moment along this mode (Table 2). Our most accurate prediction of the vibrational averaged PA values at the fundamental and overtone states are 31 and 36 meV, respectively, which strongly supports the conclusion that a positron can bind to formaldehyde (Figure 7).

<table>
<thead>
<tr>
<th>ν</th>
<th>PA&lt;sub&gt;ν&lt;/sub&gt; [meV]</th>
<th>μ&lt;sub&gt;ν&lt;/sub&gt; [debye]</th>
<th>α&lt;sub&gt;ν&lt;/sub&gt; [Å&lt;sup&gt;3&lt;/sup&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td>gs</td>
<td>25.78(3)</td>
<td>2.80</td>
<td>2.46</td>
</tr>
<tr>
<td>1&lt;sub&gt;1&lt;/sub&gt;</td>
<td>24.51(3)</td>
<td>2.76</td>
<td>2.51</td>
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<tr>
<td>2&lt;sub&gt;1&lt;/sub&gt;</td>
<td>30.69(3)</td>
<td>2.83</td>
<td>2.48</td>
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<tr>
<td>3&lt;sub&gt;1&lt;/sub&gt;</td>
<td>26.03(3)</td>
<td>2.80</td>
<td>2.47</td>
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<td>4&lt;sub&gt;1&lt;/sub&gt;</td>
<td>24.88(6)</td>
<td>2.77</td>
<td>2.47</td>
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<td>5&lt;sub&gt;1&lt;/sub&gt;</td>
<td>23.60(2)</td>
<td>2.74</td>
<td>2.51</td>
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<tr>
<td>6&lt;sub&gt;1&lt;/sub&gt;</td>
<td>25.91(2)</td>
<td>2.80</td>
<td>2.47</td>
</tr>
</tbody>
</table>

* X denotes normal mode: symmetric C–H stretching (1), C=O stretching (2), CH<sub>2</sub> bending (3), out-of-plane bending (4), anti-symmetric C–H stretching (5), and CH<sub>2</sub> rocking (6) modes. The quantum number for the mode X is denoted as subscript, and for other modes, quantum numbers are set to zero.

![Figure 7 Vibrationally averaged positron affinity fit as described by eq. (4), using the dipole moment (μ<sub>ν</sub>) and polarizability (α<sub>ν</sub>) for CH₂O. The ν<sub>2</sub> denotes vibrational quantum number for C=O stretching mode, and PA(LSQ) denotes the value calculated using Eq. (4). The adjusted coefficient of determination (R<sup>2</sup>) for this fitting is also shown in this figure.](image)

2.5. References

3. Co-workers
Dr. Yukiumi Kita, Dr. Yukio Kawashima, Dr. Kenta Yamada (Yokohama City Univ.)
Mr. Masashi Daido, Mr. Katsuhiko Koyanagi, Ms. Yurika Yamada (Students)

4. Outreach
4.1. Selected publication (Total 63 papers)

14. Y. Ogata, M. Daido, Y. Kawashima, and M. Tachikawa, "Nuclear quantum effect on


### 4.2. Cover gallery

![Reference Images](image1.png) ![Reference Images](image2.png) ![Reference Images](image3.png) ![Reference Images](image4.png) ![Reference Images](image5.png)

### 4.3. Invited talk (total 30)

### 4.4. Prize

1. Takayuki Oyamada, **Best Poster Presenter Award** in The 8th General Meeting of ACCMS-VO (Asian Consortium on Computational Materials Science - Virtual Organization), “Role of electron-positron correlation in positron attachment to LiH”, @ Sendai, Japan, on 7-9, November 2013.
2. Yudai Ogata, **Best student poster award** in 3rd International Conference on Molecular Simulation, “Nuclear quantum effect on OH(H2O); with ab initio path integral molecular dynamics”, @ Kobe, Japan, on 18-20, November 2013.