Abstracts
Posters
Effects of strain on gas separation properties of porous graphene

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Based on first-principles calculations, porous graphene membranes under different strain conditions are studied. It is found that the pore size and shape can be effectively manipulated by applying stress. Under a reasonable tensile stress, the diffusion rate is significantly increased for CO$_2$, moderately increased for O$_2$, and slightly increased for H$_2$. These differentiations in the diffusions open up a mean to create a controllable gas separation membrane using porous graphene.
We have studied the atomic structures and electronic properties of 0.25 ML Pt deposited on a Ge(001) surface. A Ge nanowire (NW) structure is found above the Pt-chain modified Ge(001) surface. The Pt-chain modified Ge(001) structure seems likely to be the precursor of the NW formation, in which the Pt chain is sunken into the second atomic layer of the Ge substrate and positioned at the center of two quasi-dimer rows (QDRs). The simulated STM image of the Pt-chain modified Ge(001) surface with a widened trough (WT) geometry resembles the experimental STM image which is observed after the removal of the NW superstructure. The Ge NWs with significant dimerization present a bright two-peak NW dimer simulated STM image at a sample bias of about -1.5 eV, which becomes a single peak resulting from the $\pi$ anti-bonding at a sample bias of about +1.5V. The topography of the simulated STM images and the bias-dependent imaging are in agreement with the experimental results. Quasi-one-dimensional electronic structures within the Pt chain and QDRs along the NW direction have been revealed, and a pseudogap is opened as the periodicity of the NW translates from $\times 2$ to $\times 4$, which is interpreted in terms of a Peierls instability. The coupling between the Pt chain and the Ge atoms of the QDRs is of essential importance for stabilization.

First-principle studies of molecule adsorption on graphene: The adsorption-induced band

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We perform a systematic study of simple aromatic molecules adsorption on graphene using the density-functional theory within the local-density approximation. The adsorption properties of heterocyclic molecules (B\textsubscript{3}N\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}N\textsubscript{3}H\textsubscript{3}), and monocyclic molecule (C\textsubscript{6}H\textsubscript{6}) on graphene have been investigated, as well as the adsorption energies and equilibrium distances in several molecule configurations. Our studies show that, for heterocyclic aromatic molecules, the most favorable site is that each atom of molecule cross C-C bond of graphene but for Benzene (C\textsubscript{6}H\textsubscript{6}), is one carbon atom of graphene underneath the hollow of the molecule ring. Our calculations show that molecule adsorptions can lead to band gap opening. Our results show that heterocyclic molecule are more effective for opening graphene band gap and the value is up to 62.9meV. One other reason to support our point of view is that, for heterocyclic molecules, the most stable configuration lead to biggest band gap. The reasons of molecule adsorption inducing band gap have been discussed in this article. The charge redistribution pattern play a important role in controlling band gap. Moreover, binding energy curves verse the distance between the graphene layer have been also calculated and this provide a good reference resources to experiment.
Structure and electronic properties of nitride interfaces

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Lattice-matched interfaces are desirable to reduce the defect density. However, present-day nitride devices are fabricated on the sapphire substrate without lattice matching. Hexagonal borides with lattice mismatch less than 1\% are candidates for the alternative: GaN/ZrB\textsubscript{2}(0001) interfaces well defined on the atomic scale have already been fabricated \cite{1}, and examined also theoretically \cite{2}. Such atomically clean interfaces could be utilized in order to exhibit nanomagnetism with controlled distribution of spin sites. Indeed, in diluted magnetic semiconductors \cite{3,4}, magnetic dopants tend to clusterize or segregate resulting in difficulty to increase the Curie temperature. Furthermore, the so-called d\textsuperscript{0} magnetism where magnetism is achieved without magnetic elements is of fundamental importance.

In this study, we examine the structure and electronic properties of nitride interfaces using first-principles calculations. We find that intrinsic two-dimensional d\textsuperscript{0} ferromagnetism, which is prohibited within the model-Hamiltonian approach \cite{5}, is indeed possible at lattice-matched AlN/MgB\textsubscript{2} interfaces \cite{6}. Partially occupied N $p$ states at AlN/MgB\textsubscript{2}(0001) interfaces exhibit two-dimensional spin polarization around the Fermi level, which cannot be anticipated from the atomic structure, because the N dangling bonds are apparently saturated by Mg atoms. Strong itinerant ferromagnetism comes from Hund’s coupling of the two N $p_{||}$ orbitals as well as avoided high density of states at the Fermi energy by the exchange splitting that is comparable to typical band ferromagnets. In addition, we show that this interfacial spin polarization is responsible for quantum spin transport, and may be controlled by applied gate bias voltages. Roles of metal-induced gap states \cite{7} will also be discussed.

References
Density function theory study of the oxidation of CO on W(111) surface

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The oxidation process of carbon monoxide CO on tungsten W(111) surface is investigated by density functional theory (DFT) calculation. The molecular structures and surface-adsorbent interaction energies of CO and O₂ and W(111) surface are predicted. The both Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms for CO oxidation reaction are considered in this study. The nudged elastic band (NEB) method was applied to locate transition states and minimum energy pathways (MEP) of CO oxidation on W(111) surface. Our results show the oxidation of CO on W(111) via ER mechanism both are more easy rather than LH mechanism. The electronic density of state (DOS) are calculated to explain the adsorption properties of CO oxidation process on W(111) surface.

Key words: W(111), CO oxidation, Langmuir-Hinshelwood (LH), Eley-Rideal (ER).
A transition from an insulator to a metal is observed as impurity concentration is increased in semiconductors, for example, in silicon doped with phosphorus[1]. The impurities are randomly distributed in the system, therefore Anderson localization could appear[1], and additionally, the electrons interact with each other. Both of disorder and electron-electron interaction could play an important role to this metal-insulator transition and more realistic model including these factors is required for deeper understanding of this metal-insulator transition.

In this study, Density Functional Theory with Local Density Approximation[2] is applied to take into account the electron-electron interaction. We analyse the properties by calculating a distribution of the Kohn-Sham eigenfunctions and also a sensitivity of the ground state energy to boundary conditions to show existence of the metal-insulator transition.

The band insulator – topological insulator transition in chalcogenide heterostructure

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We study Phase change in topological order of ternary chalcogenide compounds using first-principles calculations. The calculations show that it undergoes band insulator – topological insulator transition upon the variation of composition and thickness of stacking layers as well as external strain. We derive the effective Hamiltonian to explain the transition and provide the criteria required to induce the transition based on the model of interacting Dirac fermions in 1D superlattice. We discuss the implication of this study in regard to application of chalcogenide compounds which utilizes the conducting properties originated from topological insulator.
Epitaxy of graphene on the surface of Sb$_2$Te$_3$ topological insulator

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Understanding topological phase as observed in Dirac materials such as graphene and topological insulator (TI) has been a central issue in the field of condensed matter physics. Graphene and TI exhibit unique 2D electronic structures and attract great attention for potential application to electronic devices. Heterostructures of graphene and TI provide interesting platforms to explore exotic electronic and transport properties of Dirac materials.

Electronic structures of graphene in contact with TI were investigated using first-principles methods and tight-binding models. The Dirac cones of graphene on the TI surface show several interesting features including band gap-opening and splitting. By fitting the first-principles calculations to Kane-Mele tight-binding model, we analyzed the origin of the changes in the Dirac cones. We found that both intrinsic and extrinsic spin-orbit couplings are enhanced significantly due to the proximity to topological insulator Sb$_2$Te$_3$. We discuss that our results can be utilized for using graphene as a probe of transport measurement of TI surface states.
First-Principles Study of the Origin of Ferroelectricity in Orthorhombic YMnO$_3$

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Orthorhombic YMnO$_3$ is a well-known multiferroic manganite with its exotic property of the ferroelectric polarization induced by its unique spin orders. In spite of extensive experimental studies on YMnO$_3$ during the last decade, however, little progress has been made in our understanding of the ferroelectricity origin as well as the atomic mechanism behind the observed extraordinary polarization reversal. Here, in order to clarify the origin of ferroelectricity in YMnO$_3$, we investigate magnetically-induced ferroelectricity in YMnO$_3$ by means of first-principles density-functional theory (DFT) calculations by considering the spin-orbit interaction. Our first-principles DFT calculations show that the ferroelectric polarization develops along the $a$-axis of $Pbnm$ with its value 1.4 $\mu$C/cm$^2$. More importantly, the present calculations clarify the ferroelectricity origin that the magnetically-induced improper polarization is mainly caused by an exchange striction mechanism ($S_i \cdot S_j$) in the E-type phase while the contribution of polarization driven by the inverse Dzialoshinski-Moriya interaction ($S_i \times S_j$) in the bc-cycloidal phase is ignorable. We have further successfully reproduced the polarization switching by adopting a E-type spin configuration. Although the atomic displacements of Mn$^{3+}$ are very small (~0.01 Å), the off-centering distortion clearly switches its direction from (+) to (-) $a$-axis.
Topological insulating phase of GeTe induced by atomic disorder

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Topological insulating order protected by time-reversal symmetry is robust under structural disorder. Interestingly, recent studies on phase change materials like GeSbTe showed that their topological insulating order is sensitive to atomic stacking sequences. It was also shown that their structural phase transition is correlated with topological insulating order. GeTe, a well-known phase change material, is trivial insulator in its equilibrium structure. In this study, we discuss how atomic defects such as Ge tetrahedral defect observed in amorphous GeTe can change its topological insulating order based on first-principles calculations and model Hamiltonian. We also investigated the critical density of such tetrahedral defects to induce topological insulating order in GeTe. Our study will help explore hidden orders in amorphous GeTe.
Electronic Structure and Orbital Ordering of Superconductor \( \text{Hg}_x\text{ReO}_3 \)

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The electronic structures of the superconducting material \( \text{Hg}_x\text{ReO}_3 \) (\( x = 0, 1/3, 1/2, 2/3 \)) have been investigated from first principles calculations. By using the generalized gradient approximation, we show that \( \text{Hg}_x\text{ReO}_3 \) is an A-type antiferromagnetic metal. We also demonstrate an associated dxy orbital ordering on the Re sublattice driven by the two dimensional p-d hybridization over the lattice ab plane. In addition, the exchange coupling splits the dxy orbital ordering band, leading to a magnetic moment of \(~0.3\) \( \mu\text{B} \) per Re ion.
Gallium nitride surface was proposed to be one of the candidates for efficient water splitting reaction to generate the future energy source, hydrogen gas. In experiments, the water splitting reaction occurs on gallium nitride surfaces with the illumination of light ranging from ultra violet to visible light depending on the doping. However, the atomic view of the reaction mechanics is still lack in literature. In this poster, we are presenting our ab initio study of water splitting pathways on polar (0001) and non-polar (1010) GaN surfaces. The situations of water monomer, dimer, trimer, and water monolayer are considered. The energy barriers of reaction pathways are studied via climbing nudged elastic band method. The charge transfers in the reaction are analyzed as well.

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Control of Multiple CDW Phase in SmNiC2 by Magnetism & Pressure

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According to recent x-ray scattering and electrical resistivity measurements, SmNiC2 undergoes an incommensurate charge density wave (CDW) transition with \( q_1=(0.5,0.52,0) \) below \( T_{CDW}=148K \) and a ferromagnetic ordering below \( T_c=17.8K \). It is believed that SmNiC2 is a unique system showing the interplay between the CDW and the magnetic ordering because the CDW lattice modulation disappears with the magnetic ordering below \( T_c \). [1–3] Using the first principles calculation, we have investigated the electronic structures and the Fermi surface (FS) properties of SmNiC2 and their effects on the CDW transition. In the normal pressure and paramagnetic ground state, the FS and the calculated electrical susceptibility show the prominent FS nesting feature along \( q_1=(0.5,0.52,0) \) as well as \( q_R=(0.5,0.5,0.5) \). We also found that the relative sizes of nesting features are very sensitive to the change of magnetic ordering or volume. We will discuss the behavior of CDW phases under the change of magnetic transition and pressure.

Revisiting anomalous structures in liquid Ga

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The anomalous structure of liquid Ga just above melting point (T\textsubscript{m}=302K) is characterized by the appearance of a shoulder on the high-q side of the first peak in the static structure factor of the liquid. This anomalous structure has been studied for many years but the explanation for its origin is still controversial. Based on an \textit{ab initio} simulation of Ga at T=1000K, the anomalous structure was attributed to the existence of some short-lived covalent dimers, which were considered as the remnants as solid Ga melts.

Recently, with an interatomic pair potential generated by a first-principles pseudopotential theory \cite{1}, we investigate again the origin of the well-known anomalous structure of liquid Ga. The interatomic pair potential includes a soft repulsive core and long-range Friedel oscillations \cite{2}. By classical mechanic simulations with this pair potential at T= 323K, the high-q shoulder in the static structure factor and the dynamic properties of liquid Ga are reproduced in good agreement with experimental data \cite{3,4}. With bond lengths located in the extreme inner side of the soft repulsive core, short-lived dimers are indeed found in our model. But, based on our simulation results, we give several reasons that the high-q shoulder in the static structure factor is unlikely originated from these dimers \cite{4}. Instead, the high-q shoulder produced by our model is resulted from some medium-range order, which is related to the structures beyond the first shell of the radial distribution function. By comparing the static structure factors of models with the pair potential truncated at different cutoffs, we conclude that the medium-range order is mainly caused by the Friedel oscillations within a nano-scale range.

Density Functional Theory with Fractional Occupations

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We propose a density functional theory (DFT) with fractional occupations of the Kohn-Sham (KS) orbitals for the study of ground states of many-electron systems. This DFT, which contains a free parameter controlling the orbital occupation numbers, can be reduced to KS-DFT with some fixed parameter. Utilizing the local density approximation (LDA) to this DFT, improved results are obtained for systems dominated by either single-reference characters (e.g. reaction energies, equilibrium geometries) or multi-reference characters (e.g. stretched H₂ and N₂, twisted ethylene), when compared with KS-LDA. Because of its computational efficiency (similar to KS-LDA), this DFT is applied to the study of the singlet-triplet energy gaps (ST gaps) of linear acenes (up to 74-acene). Our results are in good agreement with the available experimental results, and suggest that the decay of ST gaps with the acene length be smooth and monotonic. The ST gap for the infinite acene chain is predicted to be vanishingly small (within 1 kcal/mol). Physical arguments as well as numerical results for an optimal choice of the parameter in this DFT are presented.
Strain effects on band gap of zigzag SWCNTs

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Carbon nanotubes (CNTs) have attracted increasing attention of both theoretical and applied relevance from researchers over the past decade due to their outstanding mechanical and electronic properties. The band gap of CNTs can be modified under different mechanical deformations. Several authors have reported that a metal to semiconductor transition (MST) of zigzag SWCNTs takes place under uniaxial strain. Most of the literatures note that the band gap change of zigzag SWCNTs is due to uniaxial strain. But there is little information available done on the relation between band gap changes, Fermi point shifts and circumference expansions of SWCNTs under strain. In this paper, the first-principle calculations and the zone-folding picture are used to study the band gap of strain-induced changes of zigzag SWCNTs. The expansion of the circumference of a SWCNT which is rolled up from a single sheet of graphene were evaluated and compared with band gaps of the SWCNTs. The results are given in Figure 1. The band gap variance of the zone-folding picture with the circumference expansion correction had a better agreement with the direct calculation of SWCNTs than the results without the circumference expansion correction. These findings suggest that the band gap of SWCNTs (3n, 0) opens under zero strain not only from the curvature effects but also circumference expansion. Results of this study may be important for a better understanding of the MST mechanism of zigzag SWCNTs under uniaxial strain.

FIG. 1. The strain-induced band gap changes of zigzag SWCNTs. The solid lines show the direct calculation of the SWCNTs. The dotted lines and the dashed lines are the results without the circumference expansion corrections and with circumference expansion corrections on the basis of the zone-folding picture, respectively. Negative strain is compressive strain and positive strain is tensile strain.
First-principles study of defect properties of zinc blende MgTe

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We studied the general chemical trends of defect formation in MgTe using first-principles band structure methods [1]. The formation energies and transition energy levels of intrinsic defects and extrinsic impurities and some defect complexes in zinc-blende MgTe were calculated systematically using a new hybrid scheme. The limiting factors for n-type and p-type doping in MgTe were investigated. Possible solutions to overcome the doping limitation of MgTe are proposed. The best n-type dopant is suggested to be N with nonequilibrium growth process and the best p-type dopant is suggested to be I with its doping complex $V_{Mg}^+ + 4I_{Te}$.

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Modifying the physical properties of carbon nanotubes: Chemistry on defects
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The most common point defects in carbon nanotubes are mono- and di-vacancies, of which the di-vacancy has unexpectedly low formation energy [1, 2]. The defects modify the physical and chemical properties of materials. In addition to nano-device applications, the carbon nanotubes offer new opportunities for chemical reactions due to their large surface area. Here, we compare the chemical reactivity of defective and pristine nanotubes in order to exploit the use of both defects and chemical functionalization for tuning the physical properties of carbon nanotubes. Among the functionalizing agents, the halogens and hydrogen are frequently encountered. In this work, we concentrate on Cl, F, and H adsorption on nanotube walls. We also use -SiHn radicals as adsorbates, which help us to understand the interaction of defective nanotubes with a Si substrate. Although the functionalization by these agents is sometimes undesirable, a controlled path for selective functionalization is viable [3,4].

In our ab initio density functional theory calculations for the chemical reactivity of pristine and defective carbon nanotubes that interact with halogens and hydrogen. We first investigated the H, Cl, and F adsorption on pure carbon nanotubes, and observed structural and electronic modifications. We found that H and F form very strong directional covalent bonds while Cl binds less aggressively. The structural deformations are strong in H and F functionalized carbon nanotubes. Second, we have investigated the effect of Cl, F, and H adsorption on the reconstruction of defects. The point defects in carbon nanotubes reconstruct to reduce the number of dangling bonds. However, as we find, based on our adsorption energy values, the defect sites are more reactive for halogen and hydrogen adsorption. Moreover, the atomic structures of the defects are modified by the adsorbates. This atomic rearrangement is followed by electronic structure modifications. We find that some of the defect levels can be eliminated by exposing the nanotubes to halogens or hydrogen. We speculate that halogen and hydrogen chemistry can be used to probe defects, and also tune the electrical and thus optical properties of nanotubes. The silane-based radicals bind to defective carbon nanotubes with several configurations following the structural transformations of the radical. Our total energy results show that bonding between the carbon nanotube and a Si substrate is improved at defect sites.

Electronic properties of graphene/nanoribbon superlattices

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Abstract

The low-energy electronic properties of graphene and nanoribbon superlattices are investigated by density-functional theory. The armchair ribbon is lying on the monolayer graphene. The interlayer atomic interaction affects the low-energy electronic properties, and it makes the ribbon curves. The energy dispersion is dependent on the stacking configuration (AA and AB), the ribbon width and the existence of hydrogen atoms at the ribbon edge. The interlayer interaction modified the low-energy dispersion of the graphene/ribbon system. A band gap was opened for the AB-stacked configuration, while a gap was created for AA stacked one with particular width of ribbon. A \(3m+n\) rule for the armchair ribbon is still trackable as armchair ribbon on a graphene sheet.
MnFe$_2$O$_4$ in Single-Valence State

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Distinct from the pure normal spinel (e.g. ZnFe$_2$O$_4$ and CdFe$_2$O$_4$) and the pure inverse spinel (e.g. NiFe$_2$O$_4$) materials, MnFe$_2$O$_4$ (MFO) generally crystallizes in a mixed phase consisting of both the normal and inverse spinel structures with the fitted experimentally determined saturation moments of 5 and 3 $\mu$B per formula respectively. It is one of the iron spinels which are widely used in the microwave and magnetic recording applications characterized by high impedance and low core loss. Recent applications of MFO include cancer detection via magnetic resonance imaging and promising cancer remediation therapy like drug delivery using MFO nanoparticles. In addition to the particular partial inversion in the cation distribution is the not-yet-settled issue of the magnetic property in MFO, and accordingly the electronic valences of cations in MFO.

Employing the first-principles density-functional methods with the generalized gradient approximation for the exchange-correlation energy functional and the on-site Coulomb effect, we demonstrate, through exploring this material in various cation distributions and magnetic orders, that a collinear model in magnetism can lead to the saturation moment consistent with experimental observations. The magnetic moment of this material can be accounted for by the high-spin Mn$^{2+}$ cations at the tetrahedral site in the normal spinel structure and by the low-spin Mn$^{2+}$ cations at the octahedral site in the inverse spinel structure, i.e. supporting the single-valence state for this material. The corresponding energetics, exchange interactions and electronic properties are also presented and discussed.

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Investigation of possible half-metal material on double perovskites Sr$_2$BB'O$_6$ ($B, B' = 3d$ transition metal) by first-principle calculations.

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Abstract

We investigated the possible candidates of half-metal (HM) material in double perovskites structure Sr$_2$BB'O$_6$ ($B, B' = 3d$ transition metal). We did electronic structure calculations based on density functional theory (DFT) with both generalized gradient approximation (GGA) and GGA+$U$ approaches, where $+U$ is on-site Coulomb interaction correction. We found that there are 5 promising candidates of HM material, which are Sr$_2$ScCrO$_6$, Sr$_2$TiCoO$_6$, Sr$_2$MnCrO$_6$, Sr$_2$ZnMnO$_6$, and Sr$_2$ZnFeO$_6$. 
Ab initio prediction of superconducting transition temperature based on density functional theory for superconductors

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It is of fundamental importance to evaluate superconducting transition temperature without relying empirical parameters. Recent development of density functional theory for superconductors (SCDFT) [1] enables us to calculate the critical temperature from first principles. In the framework of SCDFT, we construct BCS-like gap equation from functional derivatives of the free energy functional with respect to the superconducting order parameter. And we predict the transition temperature from the variation of the gap function $\Delta_{nk}$ obtained by solving this equation. Although $\Delta_{nk}$ has no physical meaning, $\Delta_{nk}$ at the Fermi level approximately equals to the true gap measured from tunneling experiments.

In this work, we develop numerical codes based on SCDFT for ab initio prediction of the superconducting transition temperature. To solve SCDFT gap equation numerically, we sample rather large number of electronic states near the Fermi level where phonon-mediated interaction changes rapidly. In this poster, we introduce details of implementation such as sampling/weighting procedure and some results of test calculations: gap functions and their temperature dependence for Al (FIG.1), Nb, and MgB₂.

FIG.1 $\Delta_{nk}$ for aluminum as a function of the Kohn-Sham energy (left) and its temperature dependence at the Fermi level (right).

Non-Stoner Itinerant Ferromagnetism in Low-Dimension System

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We executed the band structure calculation for one-dimensional monoatomic chains of transition metals with LDA and GW method. In the GW calculation, we recognized a spin-dependent band width narrowing, which can be induced by the pair hopping in the extended Hubbard model suggested by J.E. Hirsch [1]. Comparing the band structure and magnetization of the monoatomic chain and the model Hamiltonian in one dimension, we suggest that the spin-dependent band width narrowing can be enhanced in low dimensional system. We suggest that the non-Stoner itinerant ferromagnetism can be observed in one-dimensional monoatomic chains of transition metal.

Gapless Band Structure of PbPdO$_2$: A Combined First Principles Calculation and Experimental Study

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Abstract

Materials can be broadly classified into metals, insulators, semiconductors, and half metals, depending on their electronic band structures. If the conduction and valence band edges meet at the Fermi level, the material belongs to a new class of solids named gapless semiconductors or zero-gap materials. Recently, the theoretically proposed PbPdO$_2$ with a zero-gap band structure to be the first oxide based gapless semiconductor. With the unique band structure, physical properties of PbPdO$_2$ are very sensitive to external influences, such as pressure or magnetic field, or internal forces. We present experimental evidence of the gapless band structure of PbPdO$_2$ by combined x-ray photoemission and x-ray absorption spectra complemented with first principles band structure calculations. The electronic structure near the Fermi level of PbPdO$_2$ is mainly composed of O 2$p$ and Pd 4$d$ bands, constructing the conduction path along the Pd-O layer in PbPdO$_2$. Pd deficiency in PbPdO$_2$ causes decreased O 2$p$-Pd 4$d$ and increased O 2$p$-Pb 6$p$ hybridizations, thereby inducing a small band gap and hence reducing conductivity. Hall measurements indicate that PbPdO$_2$ is a p-type gapless semiconductor with intrinsic hole carriers transporting in the Pd-O layers.
One-side dehydrogenation of *graphane* by asymmetric laser pulse

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*Graphane* is hydrogen (H) terminated graphene on both sides of the sheet forming \(sp^3\)-like bond network. *Graphane* was theoretically proposed in 2007 [1] which was experimentally formed later[2,3]. The graphene sheet consists of A and B sites of carbon (C) atoms. Meantime, in *graphane*, all these sites are terminated by H atoms; A-site is terminated by H-atom from one side of the graphene sheet while the B-site is terminated from the other side of the sheet. Since C-H bonds on both side has the same binding energy, it is thermodynamically difficult to desorb H atoms only from one side.

In this paper, we propose non-thermal way to desorb H atoms only from one-side of *graphane*. Figure 1 shows the first-principles simulation of the molecular dynamics based on the time-dependent density functional theory[4], representing H-desorption only from upper side of *graphane*. We assume very short (\(\sim\) 2 fs) pulse laser causing asymmetric time-variation of the electric field of laser shot. This asymmetric laser shot causes large driving forces to H atoms on one side while causes small driving forces to H atoms on the other side.

We will present details of the numerical scheme [5,6] to perform this simulation and discuss application of the ultra-short laser pulse for structural change of materials as well as possible applications of the half-dehydrogenated structure.

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Theoretical investigation on the interaction between carbon monoxide and carbon nanotubes with single vacancy defect [1]

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Among various known synthetic procedures, the chemical vapor decomposition (CVD) of CO molecules on metal nanoparticles \cite{2} has been shown to be able to induce higher efficiency for CNT growth and easier control of the growth conditions. Yet, all of the available laboratory studies on the mechanism of CNT growth have only indicated that the CO molecules are the carbon sources to precipitation of amorphous carbon by thermal self-decomposition. In this work, we study the possibility of healing the defective carbon nanotube (CNT) by CO molecules. The healing processes undergoes three steps: (i) the chemisorption of the first CO molecule on CNT, (ii) the incorporation of the C atom of CO into the CNT, accompanied by the adsorption of the leaving O atom on CNT, (iii) the removal of the O atom from the CNT by a second CO molecule, forming perfect CNT and CO\textsubscript{2} molecule. Overall, adsorption of the first CO molecule will overcome the barrier of 2.99 kcal/mol and release the large energy of 109.11 kcal/mol, while adsorption of a second CO molecule needs overcome the intrinsic barrier of 32.37 kcal/mol with the exothermicity of 62.34 kcal/mol. In general, the barrier for the second CO molecule’s adsorption is hard to be overcome at room temperature. However, in light of the unique synthetic condition of CNT, such as high temperature and closed container, the healing processes could be effective. Therefore, we propose that among the chemical vapor decomposition of CO on metal nanoparticles for CNT growth, the CO molecule can not only act as the source of carbon, but also as the “healer”.

The potential energy surface for the adsorption of the CO molecules on defective CNT

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Crystal structure prediction: a novel approach based on minima hopping

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Reliable structure prediction of periodic systems is essential when searching for novel solid state phases or entirely new materials and their physical properties. With increasing computational resources the search for novel crystal structures from first principle calculations has become feasible, but still remains a demanding task. Commonly, enthalpically favorable structures are extracted from databases of structures found in similar materials. However, this approach has a limited success rate when the ground state is an unknown structure, which can only be found by performing an educated guess based on chemical intuition.

Recently, more advanced methods for crystal structure prediction have been developed and successfully applied to various materials. They allow a systematic search for the ground state structure based solely on the system's composition. These methods include simulated annealing\([1]\), genetic algorithms\([2]\), constrained random search methods\([3]\) and metadynamics\([4]\). Motivated by the promising results of the minima hopping method\([5]\) obtained on isolated systems, we have generalized the algorithm for crystal structure prediction\([6]\). Optimized moves in the configurational space spanned by both atomic coordinates and simulation cell variables are performed to escape from local enthalpy minima, and revisiting known minima is avoided, thus allowing a fast exploration of the enthalpy surface. Results on the prediction of new superconducting phases in hydrogen rich materials and of the structure in cold compressed graphite are presented based on first principle calculations.

Stability and electronic structure of donor-pair defects in Si$_{1-x}$Ge$_x$ alloy nanowires

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Semiconductor nanowires (NWs) have attracted much attention because of their potential applications for future nanoscale optical and electronic devices. Although impurity doping is important for practical applications, it is generally difficult to dope nanowires due to several reasons. Dopant impurities are abundant near the surface of NWs. The activation energies of dopants are higher than those in bulk materials because of the low dielectric screening and quantum confinement effect. Charge carriers are compensated by surface defects, such as dangling bonds. Moreover, electrically inactive donor-pair defects also reduce the activation of dopants, especially in small-diameter NWs [1].

In this work we investigate the defect properties of P dopants in Si, Ge, and Si$_{1-x}$Ge$_x$ alloy NWs through density-functional theory calculations [2]. When the wire diameter is below a critical value, P dopants tend to form donor-pair defects, which consist of two dopants at the first nearest distance. The stabilization of donor-pair defects against isolated substitutional donors is affected by the quantum confinement and chemical bonding effects. In small-diameter NWs, the donor-pair defect has a deep anti-bonding level in the band gap which is fully occupied and electrically inactive. As a result, the doping efficiency is greatly reduced in small-diameter NWs. The formation of donor-pair defects becomes more favorable as the Ge composition ratio increases, which is attributed to the increase of the conduction band minimum state. Thus, the doping efficiency of P dopants will be lower in Ge and Si$_{1-x}$Ge$_x$ alloy NWs, as compared to Si NWs. We also present the results of hybrid density functional calculations for the band gap of NWs and the doping efficiency.

Boron segregation and effect of point defects in Si/SiO₂ interface

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Boron is one of $p$-type dopants in metal-oxide-semiconductor field-effect transistors (MOSFETs). However, it is not easy to control the profile of B dopants in MOSFET devices because of the transient enhanced diffusion, B clustering, and B segregation to Si/SiO₂ interface. As downscaling of the device continues, B segregation at Si/SiO₂ interface becomes more significant. Thus, it is important to understand the mechanism for B segregation at the atomic level.

In this work, we perform first-principles density-functional calculations to study the mechanism for B segregation in Si/SiO₂ interface. We generate three interface structures between crystalline Si and amorphous SiO₂ ($a$-SiO₂) using first-principles melt-and-quench molecular dynamics simulations. We find that B is energetically more stable in amorphous SiO₂ as an interstitial defect, compared with a defect complex of B with a Si self-interstitial in Si. In the absence of point defects, an interstitial B forms a complex with two B-O bonds and one B-Si bond in $a$-SiO₂. When point defects such as Si floating bonds and Si-Si dangling bonds are generated, the stability of B is greatly enhanced, especially near Si floating bond defects. Thus, Si floating bond defects act as B traps in $a$-SiO₂. On the other hand, Si-Si dimer bonds do not significantly affect the stability of B.
Schottky barriers and work functions of Ni/HfO$_2$ and Ni/SiO$_2$ gate stacks

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Recently, high-k/metal gate stacks have been used as the replacement of poly-Si/high-k gate stacks in conventional complementary metal-oxide semiconductor (CMOS) devices because gate leakage current and poly-Si depletion are significantly suppressed. In high-k/metal gate stacks, the work functions of metals should match to the doping levels of poly-Si gate, 4.05 eV for $n$-type electrode whereas 5.15 eV for $p$-type electrode. However, when high-k/metal gate interfaces are formed, the metal work functions are commonly affected by interface dipoles and defects. Thus, it is important to control the effective work function in CMOS devices based on high-k/metal gate stacks.

In this work, we perform first-principles density-functional calculations to study the Schottky barriers and metal work functions in Ni/HfO$_2$ and Ni/SiO$_2$ interfaces. We use the generalized-gradient approximation (GGA) for the exchange-correlation potential and the projector-augmented wave potentials. From the local density of states, we estimate the Schottky barrier height. In addition to the metal induced gap states, we find the localized interface states which are formed in the interfacial O layer. The characteristics of the localized interface states are different between Ni/HfO$_2$ and Ni/SiO$_2$ interfaces. We also examine the effects of O-vacancy defects at the interface, and find that the Schottky barrier height in Ni/HfO$_2$ interface increases with increasing of the defect density, while the effect is negligible in Ni/SiO$_2$ interface. The difference between two interfaces is attributed to the different charge transfers at the interface. We discuss the limitations of GGA and the advanced approaches such as hybrid density functional and quasiparticle $GW$ calculations.
Magnetism during adsorption of O$_2$ on Pt segregated Pt$_3$Ni (111): Density Functional Study

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ABSTRACT

Limited understanding of the surface properties of Pt$_3$Ni for the oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cell (PEMFC) has motivated the study of magnetic properties and electronic structures of Pt segregated Pt$_3$Ni (111) surface during adsorption of oxygen molecule on it. The first principle method based on density functional theory (DFT) is carried out. Nonmagnetic Pt has induced magnetic moment due to strong hybridization between Ni 3d and Pt 5d. It is found that an oxygen molecule prefers bridge site with Pt rich subsurface environment for adsorption on the surface of Pt segregated Pt$_3$Ni (111). We found that there is very small charge transfer from O$_2$ to Pt. The magnetic moment is mainly coming from the oxygen molecule. The curve of energy versus magnetic moment of the oxygen explains the physical phenomena. The spin polarized densities of states are presented in order to understand physical properties of Pt and O$_2$ during the adsorption in detail.

Keywords: Fuel cell, Pt$_3$Ni, density functional theory, magnetic properties, electronic structure
Carbon vacancies are the most common defects in carbon nanotubes and graphene and significantly affect to their electronic and transport properties. Vacancy defects can be generated under ion irradiation, and the type of defects can be controlled by irradiation energy or thermal annealing.

In this work, based on first-principles matrix Green's function calculations, we study the effect of various carbon vacancies on the electrical conductance and the Anderson localization induced by disorder in (5,5) and (9,0) carbon nanotubes. For small vacancy clusters $V_n (n \leq 6)$, where $n$ is the number of missing atoms, the conductance near the Fermi level exhibits an oscillatory decreasing behavior. The suppression of conductance is associated with the defect states, $\pi$-topological defects for $n = \text{even}$ whereas $\sigma$-dangling bond defects for $n = \text{odd}$. As vacancies aggregate into larger vacancy clusters $V_n (6 \leq n \leq 36)$, the conductance near the Fermi level decreases exponentially with increasing of $n$ mainly due to the local gap opening. In disordered nanotubes with a small amount of vacancy defects $V_n (n \leq 4)$, the conductance also exhibits the exponential decreasing behavior due to the Anderson localization. We find that the localization length not only depends on the type of vacancy defects but also on the tube chirality.
Magnetic Interactions in Fe-doped TiX₂ (X=S, Se)

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TiX₂ (X=S, Se) share the same type of crystal structure. Their physical properties, however, are different from each other. While TiSe₂ bears an unconventional charge-density wave (CDW) transition under 200K, TiS₂ shows no distinct structural distortion.[1] Furthermore, iron-intercalated TiS₂ and TiSe₂ exhibit different types of magnetism. While Fe₀.₅TiS₂ shows a ferromagnetic ordering under 80K, Fe₀.₅TiSe₂ bears an antiferromagnetic ordering under 135K.[2,3] In order to describe the magnetic interactions between Fe atoms, we apply the first principle calculation on FeₓTiX₂ (X=S, Se) supercells. We also discuss on the pressure effect in the compounds.


Critical Evaluation of the LDA + U Approach for Band Gap Corrections in Point Defect Calculations: The Oxygen Vacancy in ZnO Case Study

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The LDA+U approach can be used essentially as band gap correction for defect study. This approach was previously applied to the oxygen vacancy in ZnO by Paudel and Lambrecht [1]. Here, we review the nature of the LDA+U method and introduce additional refinements. The U values were adjusted to reproduce as closely as possible the band structure of ZnO in the QSGW approach. The new LDA+U model applied to the oxygen vacancy in ZnO. Good agreement is obtained with recent hybrid functional calculations on the position of the 2+/0 transition state. A comparison of various approaches on the oxygen vacancy in ZnO is provided. The relevance of the one-electron levels to the experiments is discussed.

Origin of huge difference in the vibrational spectra between OH’(H2O)$_3$ and OH’(H2O)$_4$ clusters

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In many studies, vibrational spectra are used as powerful probes to reveal the hydrogen bonded network in the liquid water and ice, and the role of ions in aqueous phase. However, the full understanding and assignment of observed spectra is still controversial. On the other hand, if one turns to small water and hydrate clusters it should be possible, in principle, to assign all the peaks seen in the experiment, and furthermore, one may hope that theory could simulate the spectra without any empirical corrections.

In this study, we perform ab initio theoretical simulation for the vibrational spectra of hydroxide anion clusters, OH’(H2O)$_3$ and OH’(H2O)$_4$, to confirm the origin of the huge difference of experimental spectra between these clusters.$^{[1]}$ As the first step, we solve the vibrational problems as the eigenvalue problem using the potential energy surface(PES) and dipole moment function(DMF) of adiabatically separated waters and OH$^-$ units with B3LYP. Inter units coupling effect is also included by expanding the total vibrational Hamiltonian by direct product basis functions. Moreover, to directly simulate the shape of the experimental spectra, both the homogeneous and inhomogeneous widths of the spectra are estimated using the on-the-fly classical dynamics calculations and rotational constants information.

Through these simulations,$^{[2]}$ we show that the dominant conformer of OH’(H2O)$_4$ should be the one with a second solvation shell water as suggested by Robertson et al.$^{[1]}$ Our simulated spectrum of this conformer reproduce the experimental spectrum well including the complex behavior in the energy region governed by the second shell water OH bands. Furthermore our results clary show that, rather than the second shell water OH bands themselves, the inter water OH stretching of the first shell water connecting to the second shell water as the donor is essential to determine the dominant conformer in experiment.

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First-principles calculation of transport properties of Al/GaN interface

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Gallium nitride (GaN) is a wide bandgap semiconductor attracting significant attention due to its possible applications to semiconductor devices such as diodes, LEDs and solar cells. Since semiconductor devices are always contacted with metallic electrodes, transport properties of metal-semiconductor interfaces are vitally important for device development. One troublesome phenomenon is the Schottky barrier generated in the interface that prevents current flow and reduces device performance. Hence a large number of experimental efforts have been made to minimize this effect when a new device is developed. For more efficient developments of devices, introducing quantum simulations based on first-principles calculations is one of the most promising techniques.

A heterojunction like metal-semiconductor interface can be considered as a multilayered system since there exists a two-dimensional translation symmetry within a plane parallel to the interface. It however is still difficult to calculate the electronic states of multilayered structures by first-principles calculation. It is because that the unit cell to be dealt with is elongated along one-direction and thus contains many atoms, which makes the computational cost rather high.

The screened KKR method \cite{zeller1995} can solve the Kohn-Sham equations efficiently especially for multilayered systems. Furthermore, by implementing the Kubo-Greenwood formula \cite{butler1985} into the screened KKR, we have realized fast first-principles calculation of the conductivities of multilayered systems.

In this presentation, we will show the results of our recent calculations on the transport properties of Al/GaN contacts. This is a new application of our method to materials design of GaN devices.

\begin{thebibliography}{9}
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New structural model for Na$_6$Si$_3$ magic cluster on Si(111)-7x7 surface

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In this study, the new Na$_6$Si$_3$ magic cluster structure on the Si(111)-7x7 surface were discovered by using density-functional theory. Our new structural model of Na$_6$Si$_3$ magic cluster is more stable (0.282 eV less) than the triangular Na$_6$Si$_3$ model (See Fig. 1a) reported by Kehui Wu et al. [Phys. Rev. Lett. 91, 126101 (2003)]. The triangular Na$_6$Si$_3$ model has three Na atoms (purple ball) adsorbed on the sites neighboring Si rest atoms (blue ball), the other three Na atoms occupy the center T4 and bridge sites, and the original three Si atoms on the center T4 sites diffuse to the center of half-unit-cell to form a Si trimer. However, the most stable site for single Na atom is at the bridge sites between the rest atom and centered backbone atoms. By putting the Na atoms at the six symmetry equivalent positions, it will form a hexagon Na$_6$Si$_3$ model (see Fig 1b). Our results reveal a more stable Na$_6$Si$_3$ model which has six Na atoms with hexagon shape as hexagon model, but three center Si adatoms are diffused to the center of half-unit-cell to form a Si trimer as triangular model, and thus we called this new model as hexagon-triangular model as shown in Fig. 1c. The total energy of hexagon-triangular model is 0.282 eV lower than triangular model and 0.518 eV lower than hexagon model. The simulated STM images of hexagon-triangular model are found better than the triangular model when compared with experimental STM observation. We conclude that the hexagon-triangular model is the true configuration for the Na$_6$Si$_3$ magic cluster on Si(111)-7x7 surface.

![Fig. 1 Three structural models of Na$_6$Si$_3$ magic cluster on Si(111)-7x7 surface. The white, red, blue, and purple balls represent Si backbone atoms, Si adatoms, Si rest atoms, and Na atoms, respectively.](image-url)
Interaction between Nitrogen Dopants and Native Point Defects in Graphene

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To understand the interaction between nitrogen dopants and native point defects in graphene, we have studied the structural relaxation, energetic stability, and electronic structures of N-doped graphene with vacancies and Stone-Wales (SW) defect by performing the density functional theory calculations. Our results show that N substitution energetically prefers to occur at the carbon atoms near the defects, especially for those sites with larger bond shortening, indicating that the defect-induced strain plays an important role in the stability of N dopants in defective graphene. In the presence of mono-vacancy, the most stable position for N dopant is the pyridine-like configuration while for other point defects studied (SW defect and di-vacancies) N prefers a site in the pentagonal ring. Our results also show that the native point defect and N dopant attract each other, i.e., cooperative effect, which means that N dopants can prompt the creation of point defects and vice versa. This is supported by the increasing intensity of D-band in the Raman spectra of N-doped graphene and also by the controllable N doping of graphene that has been realized by the NH₃ annealing of graphene after N⁺ -ion irradiation or by the NH₃ plasma exposure of graphene. The electronic structures of the N dopant-defect complexes are analyzed. It is found that the pyridine-like N at mono-vacancy has a lone pair of σ electrons and two N dopants (pyridine-like N plus a substitutional N at a pentagon ring) are needed to compensate one hole induced by a mono-vacancy.

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Electron transport through molecular junctions with thiolate–Au and carboxylate–Cu anchoring bonds

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Although a thiolate–Au bond has been well-known as a preferable anchoring group to bind molecules on a Au surface, Lennartz et al. have proposed a carboxylate–Cu bond as an alternative [1]. The electron transport via the carboxylate–Cu bond is still unclear, and the difference from that via the thiolate–Au bond is the focus of scientific attention. We present a theoretical study on the difference in electron transport through molecular junctions with anchoring bonds between the base group and metal surface.

Using a density-functional code based on the real-space finite-difference method, we evaluate the electronic structures of benzenedithiolate (BDT) and terephthalate (TPA) molecular junctions [Fig. 1(a)-(b)]. Their electron transmissions are calculated using an electron transport code also based on the real-space finite-difference method.

Figure 1(c)-(d) show projected density-of-states (PDOS) with respect to atomic orbitals. Electronic states are hardly observed at the C atoms in the carboxylates of the TPA junction, implying break-up of the electronic states at the C atoms. In the BDT junction, the electronic states are observed to bridge over the S atoms. The electron transmissions of the junctions [Fig. 1(e)] reflect the features observed in the electronic structures; i.e., the electron transmission of the BDT junction is smooth, while that of the TPA junction is sharply-peaked. The difference in the transmissions can be interpreted as that forbidden energy bands exist locally at the C atoms in the carboxylates and the local electronic structures form a quasi-double-barrier structure across the TPA junction, where energy-sensitive resonant electron transport may occur.

Figure 1: (a)-(b) are models of the BDT and TPA junctions. (c)-(d) show PDOS, and the PDOS for $s$ orbitals are faint and unobservable. (e) shows the electron transmissions.

Ab initio studies of structural and electronics properties, spin waves and exchange interaction, and Curie temperature in bulk Gadolinium

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We have studied the structural and electronics properties of gadolinium in hexagonal-closed-packed (hcp), face-centered cubic (fcc) and double hexagonal-closed packed (dhcp) structures using the GGA and the Vienna ab initio simulation package (VASP). For the GGA, we used both GGA-PW91 and GGA-PBE. Due to the strong on-site Coulomb interaction in 4f electrons, we also performed the GGA+U calculations in the Dudarev’s approach with effective Coulomb U = 6 eV. The structural relaxation calculations with GGA-PW91+U show that the ferromagnetic hcp phase is the ground state of Gd. The calculated structural parameters for the hcp phase are in good agreement with the experimental axial ratio c/a = 1.597 Å and lattice parameter a = 3.642 Å. In contrast, all the other exchange-correlation potentials (GGA-PW91, GGA-PBE, and GGA-PBE+U) predict the antiferromagnetic state to be the ground state which is inconsistent with experiments. We discuss the band structure of hcp, dhcp and fcc Gd. Using the experimental lattice constants, we performed noncollinear magnetism and spin spiral structure to investigate the magnon dispersions. This work shows that there are both branches of acoustic and optical magnons. We evaluate the exchange interactions from calculated magnon dispersions in the frozen magnon approach. The Curie temperature has also been calculated in both mean field approximation and random phase approximation.
Structural and Magnetic Phase Transition of Fe, Co and Ni under Anisotropic Compression

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The structural and magnetic phase transition of Fe, Co and Ni under anisotropic compression, i.e. $P_x=P_y \neq P_z$, is investigated by the density functional based methods.

Fe was found to transit from ferromagnetic (FM) BCC structure to nonmagnetic (NM) HCP structure at 3.1GPa and then to NM FCC at ~180GPa when under epitaxial compression ($P_x=P_y \neq P_z =0$). The experimentally observed hydrostatic phase transition of Fe from FM BCC to NM HCP at ~13GPa was also predicted.

The pure structural transition of Co from FM HCP to FM FCC was found under epitaxial compression of ~75GPa and from FM HCP to FM FCC under uniaxial compression ($P_x \neq P_y=P_z =0$) of 1.9GPa and further to FM BCT at 3.9GPa.

For Ni, we observe the pure structural phase transition of Ni from FM FCC to FM BCT under uniaxial compression at 3.5 GPa and the pure magnetic phase transition under epitaxial compression from FM FCC to NM FCC at ~175GPa. The crucial mechanisms behind all these phase transitions are also studied and presented.

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Ab Initio Studies of Electronic Structure, Magnetism and Ferroelectricity in BiMnO$_3$

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Abstract

Solovyev and Pchelkina [1] recently proposed that the C2/c symmetry in BiMnO$_3$ is spontaneously broken by hidden noncollinear antiferromagnetic order and becomes the Cc one with ferroelectric polarization, based on their low energy model derived from ab initio electronic structure calculations [2]. Here we investigate the stability of the various magnetic structures and associated ferroelectricity by ab initio noncollinear and relativistic electronic structure calculations using highly accurate full-potential projector-augmented wave method. The calculations show that the hidden antiferromagnetic state AFAF could indeed be the ground state and gives rise to the observed ferroelectric polarization.

Reference

Revisiting the mechanism of photocatalytic activities in N-doped TiO$_2$

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Photocatalysis has attracted much attention because it possesses a great potential for environmental remediation and fuel production [1]. TiO$_2$ has been a major player in this field since the discovery of water splitting on Pt-loaded TiO$_2$ under ultra violet, i.e. Honda-Fujishima effect [2]. Nitrogen doping was found to be effective for activating TiO$_2$ under visible light [3], but its mechanism is still under debate [4-7]. In this work, we have challenged the longtime riddle “Why does nitrogen doping in TiO$_2$ can contribute to photocatalytic activities even though a deep impurity state is known as disadvantageous for photocatalysis?”. Nitrogen doped TiO$_2$ is a well-known visible-light sensitive photocatalyst where deep impurity states associated with substitutional nitrogen at oxygen sites (N$_O$) are believed to be the source of the red shift in photo-absorption edge [4-6]. However, such a deep level should trap hole carriers, degrading oxidation process. The contradiction between the deep N$_O$ level and rather a high oxidation power of N-doped TiO$_2$ has been an unsolved puzzle.

Here, we propose a convincing mechanism which successfully solves the riddle. N$_O$ strongly binds with a titanium atom at an interstitial site, forming a defect-impurity band, which consists of bonding and anti-bonding states between nitrogen $p$ and titanium $d$ and narrows the band gap. Such a newly formed band, which is connected to the valence band maximum of the host TiO$_2$, becomes the migration path of photo-induced hole carriers, assisting carrier transfer to the surface. This clearly explains the photocatalytic activity of N-doped TiO$_2$ both for the visible-light absorption and oxidation reaction with hole carriers [8]. This work was supported by the JSPS KAKENHI (21760030) and the JST PRESTO program.

[1] Hua Tong, Shuxin Ouyang, Yingpu Bi, Naoto Umezawa, Mitsutake Oshikiri, and Jinhua Ye, Advanced Materials DOI: 10.1002/adma.20110275
[8] Naoto Umezawa and Jinhua Ye, unpublished
We apply a quantum walk[1] of electronic wavefunction in order to evaluate the time progression of the spatial probability distribution in the Hilbert space $H_p \otimes H_c$ where $H_p = \hat{I}^2(Z)$ is associated with the position and $H_c = C^2$ with the internal degree of freedom (spin). A quantum walk of an electron represented as a wavefunction in real space as a probability distribution, provides the time evolution of the wavefunction which is a solution of time-dependent Schrödinger equation (TDSE) of the electron. When the initial distribution of the position for the electron is sufficiently wide considering the uncertainty principle limit, the quantum walk reproduces the exact solution of the TDSE. More detailed discussion on the initial condition and the boundary condition dependence will be presented in the meeting.

Multiple conical intersections in time-dependent density functional theory

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Conical intersections of molecular potential-energy surfaces play important roles in many photochemical processes. A well-known example is the “geometric (Berry) phase effect”: A geometric phase with a value of \( \pi \) is accumulated after the nuclear coordinates traverse a loop that encloses a single conical intersection; this geometric phase reverses the sign of the electronic wavefunction and has been found to be responsible for a spectrum of phenomena [1]. However, when the loop encloses multiple conical intersection points, \textit{ab initio} calculations based on correlated-wavefunction methods revealed that the geometric phase would significantly deviate from \( \pi \) [2]. Efforts are now being taken to clarify the features of this deviation to see if it is common.

In the present study we use time-dependent density functional theory (TDDFT) to explore geometric phases in the existence of multiple conical intersections. The TDDFT-based approach for calculating nonadiabatic couplings (NAC) has been recently developed, which shows both good accuracy and efficiency [3]. The geometric phase is calculated by the line integral of NAC along the loop around the intersection point. The calculation example of \( \text{H}_3 \) (\( R_{\text{H-H}}=1.0477 \text{ Å} \)) shows that the geometric phase due to the conical intersection of the ground and first excited states drops from nearly \( \pi \) to 2.21, when the loop radius is increased from 0.5 Å to 0.8 Å. This indicates the existence of the conical intersection between the second and third excited states. Our result is consistent with wavefunction-based calculations [2]. More results will be discussed in the presentation.

Recent progress in spintronics has been increasingly evoking interests in the role of spin-orbit interaction (SOI) in condensed-matter physics. SOI induces many intriguing phenomena. At surfaces, it causes spin splittings even in nonmagnetic materials. This effect was pointed out by Rashba.[1] In the present work, we study the dependence of the spin splitting on the number N of atomic layers, using QMAS [2] for first-principles calculations, for Au(111) surface.[3] When the slab of the atomic layers is sufficiently thick, the lower split state has a minimum away from $\Gamma$, as seen in the ordinary Rashba system. As the number of layers decreases, the minimum approaches $\Gamma$, and it is located at $\Gamma$ for $N \leq 14$. (see Figures below) This crossover is analyzed in detail using two models: a tight-binding model and a bilayer nearly-free-electron model. The behavior of the surface bands depend also on the strength $\lambda$ of the SOI. It is demonstrated that the features of surface band dispersion are clearly understood as the result of the competition between the interference of the surface states on both sides and the SOI. We obtain the explicit condition for the occurrence of spin-split bands in an electronic structure calculation using a slab. The insights obtained in the present work will help one to distinguish artifacts coming from the finiteness of a slab and the intrinsic properties of a surface system.

First principle study of doping HoMnO$_3$ with lone pair cations

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Rare earth manganites (RMnO$_3$) with smaller R radius (R=Ho-Lu) have a non-perovskitic hexagonal structure ground state structure in contrast to the large radius (R=La-Dy) which crystallize in orthorhombic phase [1]. Thus HoMnO$_3$ has a P6$_3$cm hexagonal ground state structure but it can be synthesized as an orthorhombic Pbnm perovskite under high temperatures and pressure. Both experimental and theoretical findings have predicted that ortho-HoMnO$_3$ has an AFM E ground state and its electric polarization is found to arise due to this specific magnetic ordering [2,3,4].

In this work a first principle attempt has been made to study the structure and properties of doping lone pair cations to HoMnO$_3$. Electronic structure calculations were carried out to study Ho$_{0.5}$A$_{0.5}$MnO$_3$ (A=Bi, Pb) under the Generalized Gradient Approximation (GGA) with and without the onsite coulomb interaction U. This attempt has been made to analyze the effect of the lone pair cations towards electric polarization and thus to predict new multiferroics.

Complete optimization was carried out for both the compounds for the different magnetic ordering (AFM A, C, G, E and FM) to predict the stable ground state structure. Under the first principle calculations Ho$_{0.5}$Pb$_{0.5}$MnO$_3$ was found to be ferromagnetic and metallic under both GGA and GGA+U implementations of DFT. Addition of divalent Pb to HoMnO$_3$ introduced holes thus leading to a metallic behavior. Ho$_{0.5}$Bi$_{0.5}$MnO$_3$ is found to be multiferroic with an antiferromagnetic E type ground state structure like the parent compound HoMnO$_3$. Thus a new multiferroic material is predicted.

Gap Opening of Bilayer Graphene by Dual Doping Method

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The band gap opening of graphene is the most desired property in device industry because it is vital to the application of graphene as a logical device of semiconductors.\textsuperscript{[1,2]} Here, we show how to make a reasonably wide band gap in graphene. This is accomplished with bilayer graphene (BLG) dual-doped with FeCl\textsubscript{3} acceptor and K donor. To elucidate this phenomenon, we employed the first principles method taking into account van der Waals interaction. For the FeCl\textsubscript{3} adsorbed BLG, the optimal distance between the adjacent graphene and FeCl\textsubscript{3} layers is 4.6–4.8 Å, consistent with experiments. Due to high electronegativity of FeCl\textsubscript{3}, these graphene layers are hole-doped. The dual-doped BLG gives band gap of 0.27eV due to broken symmetry, with Dirac point shift by -0.09 eV. This increased band gap and proper Dirac point shift could make the dual-doped BLG useful for applications towards future field effect transistor devices.

\textsuperscript{[1]} J. W. Yang, G. Lee, J. S. Kim, K. S. Kim. JPCL (DOI: 10.1021/jz201098u)
Optimization of the Jastrow factor based on pseudo-variance minimization by the transcorrelated method for solids

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In \textit{ab-initio} electronic structure calculations of solids, density functional theory (DFT) is presently the most popular method since it gives us satisfactory results in many cases with relatively low computational cost, while it is difficult for the DFT-based methods to improve their accuracy systematically. On the other hand, traditional wavefunction-based approaches have systematic ways to improve their accuracies although it is not easy to apply them to solids because of their heavy computational costs.

The transcorrelated (TC) method [1-5] is a wave-function-based approach applicable to solids in terms of the computational cost. In this method, the total wave function is approximated as a product of the Jastrow factor and the Slater determinant.

\[ \Psi_0 = F\Phi_0, \quad F = \exp(-\sum_{i<j} u(x_i, x_j)) : \text{Jastrow factor}, \quad \Phi_0 : \text{Slater determinant} \quad (1) \]

Next the Hamiltonian is similarity-transformed by the Jastrow factor,

\[ \mathcal{H}\Psi_0 = E_0\Psi_0 \Leftrightarrow \mathcal{H}_{TC}\Phi_0 = E_0\Phi_0, \quad \mathcal{H}_{TC} = F^{-1}\mathcal{H}F, \quad (2) \]

and we solve an SCF equation constructed like the HF method. It is a remarkable feature that we can optimize one-electron orbitals in the Slater determinant with relatively low computational cost comparing with other methods utilizing the Jastrow-Slater-type wavefunctions, e.g., variational Monte Carlo method. However, optimization of the Jastrow factor requires a great computational effort in solids while it is indispensable to high-accuracy calculations.

In this study, we developed a new method to optimize the Jastrow factor. We define the pseudo variance,

\[ \sigma_{PS}^2 = \sum_{i} \langle \Phi_0 | \mathcal{H}_{TC} - E_0 | \Phi_0 \rangle^2, \quad \Phi_i : \text{excited configuration}, \quad (3) \]

and use minimization of it as the guiding principle. Pseudo variance has two features: (i) nonnegative real number, and (ii) exactly zero if equation (2) holds regardless of the number of ‘i’ in the equation (3). We will show some results of test calculations and discuss how this new method works and how much the computation time of it is.

Li ion dynamics in Li$_4$GeS$_4$ and Li$_3$PS$_4$: First Principle Electronic Structure Calculation and Long Time Tight Binding Molecular Dynamics Simulation

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Sulfide type lithium super ionic conductor called thio-LISICON is one of prospective candidates for electrolytes of all-solid lithium secondary batteries, and has attracted much of attentions due to its high ionic conductivity and the viewpoint of safety. However, the lithium diffusion behavior in the thio-LISICON has not been known theoretically, though experimental studies have extensively performed. We have achieved theoretical studies by the first principle electronic structure calculation and tight-binding molecular dynamics (TB-MD) simulation for long time (nano second) diffusion behavior in thio-LISICON.

The electronic structure of Li$_4$GeS$_4$ and Li$_3$PS$_4$, e.g., the energy band structure, electron density profile in real space, the crystal orbital Hamiltonian population (COHP) and the activation energy along possible Li ion diffusion path, by using linear muffin-tin orbital (LMTO) method and first principle pseudo-potential method (ABINIT). The COHP and activation energies depend sensitively on positions of Li ions.

Furthermore, long time TB-MD simulations for 2ns are carried out in order to clarify the diffusion behavior of Li ions in the ceramic materials. The diffusion coefficient and the activation energy determined from the simulation are in good agreement with experiments. We observed that Li ions diffuse along the b(y)-axis through interstitial sites between the clusters (Fig.2).
Anisotropic Dirac-cone on the side surface of topological insulator Bi$_2$Se$_3$

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Topological insulators represent a new state of quantum matters characterized by Dirac-cone surface bands which ensures robust metallic conduction against arbitrary perturbations preserving time-reversal symmetry [1,2], and also by the helical spin texture of the surface states which leads to remarkable transport properties such as the absence of backscattering by non-magnetic defects, as confirmed by experiments [3-5].

In this poster, we will discuss the electronic structure of rhombohedral topological insulators on a ‘side surface’ defined by the Miller index (221), a new surface which has not been considered so far. We find Dirac-cone surface bands on the side surface of the topological insulator Bi$_2$Se$_3$ revealed by first-principles density-functional calculations [6], and the Dirac-cone is anisotropic in contrast to the conventional (111)-surface. We find that the electron velocity in the side surface Dirac-cone is anisotropically reduced from that in the (111)-surface Dirac-cone, and the electron spin is almost perpendicular to the wave vector $k$ where the size of the spin depends on the direction of $k$. Low-energy effective Hamiltonian is proposed for side-surface Dirac fermions, and its implications are presented including refractive transport phenomena occurring at the edges of topological insulators where different surfaces meet. This work was supported by NRF of Korea (Grant No. 2009-0081204) and KISTI Supercomputing Center (Project No. KSC-2008-S02-0004).

Coordination effects on the electronic structures of the CuA site in cytochrome c oxidase

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The CuA site was found in cytochrome c oxidase (CcO), a redox-driven proton pump in mitochondria and bacteria, and functions as a rapid intra- and intermolecular electron transfer intermediate in biological systems. X-ray crystal structures of CcO of mammalian and bacteria showed that the CuA site is a binuclear copper site, bridged by two cysteine thiolate groups. Each copper ion is coordinated by a histidine side chain and a weaker axial ligand: a methionine side chain or a backbone carbonyl group. Spectroscopic studies showed a strong σ-type bonding/anti-bonding interactions between d orbitals on each Cu in the mixed valence oxidized state due to their direct σ bonding interaction at 2.4 Å, leading to the σ_u* ground state. The σ_u* ground state shows a strongly stabilized and delocalized electronic structure which is critical in keeping the CuA site delocalized even in its low symmetry protein environment, facilitating rapid electron transfer over long distances with low driving forces.

Our goal is to elucidate what are required to make the characteristic σ_u* ground state of the CuA site. Previously, we addressed the electronic structure of the Cu2S2 core of the CuA site using the DFT methods, as the first step [1]. We found that the M06 exchange-correlation functional can be regarded as a reliable method to investigate the electronic structure of the Cu2S2 core. Our computed results demonstrate that even in the short Cu–Cu distance of 2.35 Å, the π_u state is more stable than the σ_u* state.

In this study, we have explored the effect of surrounding ligands to the stability of the σ_u*-type state and ionization and redox potentials of the CuA site in CcO through the DFT calculations. In particular, the role of each coordinating amino acid residue of the CuA site has been investigated from the viewpoint of the spin densities, charge densities, and redox potential. We discussed on the mechanism of adjustment of redox potential of CuA site by residues around core cysteine-copper part.

Study of the NMR chemical shifts of graphene clusters doped with nitrogen

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\textsuperscript{1}Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 S5-20, Ookayama, Tokyo 152-8552, Japan

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The carbon (C), hydrogen (H) and nitrogen (N) NMR chemical shifts of graphene clusters with N dopant have been studied by the first-principles electronic structure calculations. The calculations were performed with the CP2k package [1] following the prescription given by Sebastiani and Parrinello [2]. In the present work, only the local magnetic field due to orbital magnetization is included and the effects due to spin magnetic moment are left as a future work. The obtained results are summarized in the tables.

Table I: The chemical shifts of C and H (in ppm). Z, A, mono- and di-H refers to zigzag edge, armchair edge, mono- and di-hydrogenation, respectively.

<table>
<thead>
<tr>
<th></th>
<th>interior</th>
<th>Z(mono-H)</th>
<th>Z(di-H)</th>
<th>A(mono-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>edge</td>
<td>edge-1</td>
<td>edge</td>
</tr>
<tr>
<td>C</td>
<td>122</td>
<td>131</td>
<td>136</td>
<td>50</td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>7.6</td>
<td>–</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table II: The chemical shifts of N (in ppm).

<table>
<thead>
<tr>
<th></th>
<th>pyridinic</th>
<th>graphitic</th>
<th>pyridinium-like</th>
<th>pyrrolic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Z(edge-1)</td>
<td>A(edge-1)</td>
<td>interior</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>190</td>
<td>154</td>
<td>140</td>
</tr>
</tbody>
</table>

Our previous results show that N at zigzag edge-1 site can activate the nearest edge-C for oxygen reduction of reaction (ORR), and that it is difficult to distinguish N at zigzag edge-1 site from other graphitic N by the spectra of XAS, XPS and XES. However, by NMR chemical shifts of N, N at zigzag edge-1 site can be identified easily.

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Theoretical studies on a gramicidin A channel using a linear-scaling DFT technique

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Gramicidin A (gA) system is known as an ion channel, which only allows monovalent cations to permeate. The structure of gA molecule is small and simple, and the gA ion channel is important as a model membrane protein. The system has been well studied both experimentally and theoretically, and gA is the only ion channel whose atomic resolution structures were available in 1990s. In the theoretical studies of this system, classical molecular dynamics simulations have been mainly used so far, but this approach is reported to yield a large energy barrier at the channel centre, which is not in accord with experimental results. There are also other reports showing such problems of the empirical force field and it is thus important to investigate this system with the first-principles approach.

In this talk, we will report our recent study on gA systems using our linear-scaling DFT code CONQUEST (Concurrent \textit{O}(N) \textit{QU}antum \textit{E}lectric \textit{S}imulation \textit{T}echnique). The code is efficient on parallel computers and we will show that it is now feasible to carry out stable \textit{ab-initio} calculations on such a huge and complex system.

In the work, we first studied the isolated gA system to clarify the accuracy of our O(N) DFT method and to achieve the reliable calculation conditions. Some basic information, such as the effects of side chains on the atomic and electronic structures was also examined. Then, we have recently employed large-scale DFT calculations on gA channel embedded in lipid bilayers. The systems (Fig.1) we have calculated consist of gA, DMPCs for lipid bilayers, water and some ions, including more than 15,000 atoms. We will demonstrate that SCF calculations are robust and efficient even for such large and complex systems. We have calculated the atomic forces and compared them with those obtained by the classical force field, CHARMM36, and will report whether the CHARMM force field shows a good performance in this system. In particular, we will focus on the differences for the atoms near monovalent or divalent cations. The effects of the vdW interactions obtained by the DFT-D2 scheme, which is recently introduced to the CONQUEST code, will be also discussed.

Fig.1 GA system
Long-range corrected spin-orbit TDDFT calculations

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Relativistic spin-orbit time-dependent density functional theory (SO-TDDFT) is a powerful tool to include both relativistic and correlation effects with low computational cost. However, TDDFT with conventional exchange functionals have severe problems in e.g. the reproducibility of charge transfer (CT) and Rydberg excitation energies and oscillator strengths. These problems are due to the lack of long-range exchange interactions in conventional exchange functionals. We have proposed long-range corrected (LC) DFT and have overcome these problems. Especially, LC-TDDFT is the only TDDFT reproducing CT excitations quantitatively without additional operation. CT excitations usually play a major role in spin-forbidden transitions such as phosphorescence, because the SO couplings are significant for excitations inducing the changes in electron distributions as seen in the El-Sayed’s rule. In this study, the SO-LC-TDDFT has been developed to reproduce spin-forbidden transitions appropriately.

The LC-DFT has been combined with the 2-component zeroth-order regular approximation (ZORA). In the LC-DFT, the exchange energy is divided into long-range interaction and short-range interaction parts, which are represented by the Hartree-Fock (HF) exchange and exchange functional, respectively. The $\alpha-\alpha$, $\alpha-\beta$, $\beta-\alpha$, and $\beta-\beta$ long-range HF exchange energies have been evaluated in the SO-LC-DFT calculations. The short-range exchange functional has been treated in the noncollinear approach in the TDDFT calculations.

Table 1 shows the fine structures of Hg and Rn calculated by TDDFT with LDA, BLYP, B3LYP, and LC-BLYP using the Gaussian basis function optimized in the relativistic calculations. The table clearly shows that LC-BLYP reproduces spin-forbidden excitation energies and fine structures of heavy atoms with high accuracy. We also found that LC-DFT accurately reproduces the splitted Koopmans’ ionization potentials for heavy atoms.

<table>
<thead>
<tr>
<th>State</th>
<th>Hg 6s → 6p excitations</th>
<th>Rn 6p → 7s excitations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg 6s → 6p excitations</td>
<td>Rn 6p → 7s excitations</td>
</tr>
<tr>
<td></td>
<td>H 6s</td>
<td>LDA</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>0.65</td>
<td>0.61</td>
</tr>
<tr>
<td>1</td>
<td>1.77</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Theory of Chromium-doped SrTiO$_3$ photocatalyst

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In the past decades, photocatalytic activities of various semiconductors have been intensely studied for finding a prominent photocatalyst sensitized under visible light, i.e. the majority of sunlight, as an alternative material of the conventional TiO$_2$ which responses only under ultraviolet [1]. Recently, SrTiO$_3$ (STO) attracts much attention because it is harmless, stable, and economical [2]. Inspired by the lack of knowledge to understand the unique properties of chromium-doped SrTiO$_3$ (Cr-doped STO), we theoretically investigate the roles of the dopant Cr in SrTiO$_3$ based on density-functional theory with the Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional [3]. The use of HSE corrects the band gap of STO and is expected to reasonably describe electronic structure of the Cr impurity. We reveal that a Cr atom is preferably substituting for Ti (TiCr) under any equilibrium growth conditions, and the electronic structure of TiCr strongly depends on its charge state, reflecting the two major oxidation states of Cr ion, i.e. Cr$^{3+}$ and Cr$^{6+}$. Importantly, a lower oxidation state of TiCr was found to be advantageous for the photocatalytic performance of the Cr-doped STO under visible light. Our theory successfully explains the experimental results [4,5] and suggests that the desirable electronic structure is feasibly achieved by tuning Fermi level of the system.

Structural feature of entrance at a proton transfer pathway

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Although X-ray crystallography determines the relative positions of amino acid residues of proteins, the information is not necessarily enough to determine their functional roles in fundamental chemical processes such as proton transfer. This is exactly the situation encountered in the bovine cytochrome c oxidase (CcO). Namely, the X-ray structures of the bovine CcO have indicated that the side chain of Asp91, the entrance amino acid residue of one of three proton transfer pathways (D-path), is placed within the interior of the protein, yet it is well-hydrogen-bonded. It connects, via a fixed water molecule, to the side chain of His503, which is located at the molecular surface. It has been observed, on the other hand, that the side chain of His503 rotates by about 180 degree after redox reaction that causes proton transport from negative phase to positive phase. Yet, despite the experimental outcome, the role of the Asp91-His503 pair at the entrance of the D-path is still far from being unraveled.

In order to provide an insight into the relationships between the Asp91-His503 pair and its surrounding environment, we analyze, via first-principle calculations, different possible protonation states of the Asp91-His503 system during the stage in which an incoming proton is supplied to the D-pathway. We have added an additional proton to the model constructed from the X-ray structure of the fully reduced bovine CcO (17 amino acid residues and 13 crystal water molecules) and performed the geometry optimizations to determine the global and local minima for the Asp91-His503 system. We have found that an additional proton is transferred to either Asp91 or His503, leading to the formation of two different protonation states that are close in energy. The surrounding hydrogen-bonding (HB) environment has an effect essentially on both energetics and electronic structures of the Asp91-His503 system, stabilizing the formation of such a protonation state (see figure). The present calculations allow for the elucidation of the specific role played by the Asp91-His503 pair in promoting the H⁺ transfer at the entrance of the D-pathway.

Excitons at the (001) surface of anatase: Spatial behavior and optical signatures

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The discovery of the Fujishima-Honda effect [1] and the more recently invented dye-sensitized solar cells [2] have boosted the interest for the investigation of structural and optical properties of TiO\(_2\) polymorphs—rutile and anatase—in bulk, surface, and cluster systems. For what concerns the 2D systems, the most stable anatase surface, the (101) controls the crystal shape, being the reactivity governed by (001) one minority surface, source of active sites for catalytic processes. The presence of both the (101) and the (001) surfaces reveals an increased thermodynamic stability of the latter. In the last decade, different theoretical models, all supported by experimental evidences, have been proposed to explain such enhanced stability [3-6].

In an \textit{ab initio} study, based on the application of Many-Body Perturbation Theory (MBPT) approaches on top of ground-state Density Functional Theory (DFT) calculations, we investigated the optical behavior of the TiO\(_2\) anatase (001) surface [7], focusing on the (1 \(\times\) 1) and the (1 \(\times\) 4) reconstructions. Our analysis reveals a different optical response and an anisotropy, in the (001) plane, not present in the bulk phase. The determination of the spatial behavior of the e-hole photoexcited couple may explain the observed enhanced photocatalytic activity of TiO\(_2\) anatase nanostructures with a high percentage of (001)-(1 \(\times\) 1) exposed facets. Depending on the reconstruction, the character of valence band frontier orbitals gives rise to distinct behavior in optical spectra. This finding, together with the predicted optical anisotropy, should be used as a fingerprint to identify the presence of the most stable (1 \(\times\) 4) or the most photoreactive (1 \(\times\) 1) surface, in experimental samples. The spatial distribution of the photoinduced e-hole pairs reveals that the (001) orientation, mainly its (1 \(\times\) 1) unreconstructed shape, is photocatalytically efficient, with a high probability of having both carriers available for reactions taking place at the surface. We also present preliminary results and comparisons with (001) oriented anatase nanosheet and with lepidocrocite layers.

Water Contamination Effect 
on Liquid Acetonitrile / TiO$_2$ Anatase (101) Interface for 
Durable Dye-sensitized Solar Cell

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We have investigated structural and electronic properties of liquid acetonitrile (MeCN) / TiO$_2$ anatase (101) interfaces involving a water molecule in order to analyze effect of ubiquitous water contamination in the typical electrolyte solution on the durability of dye-sensitized solar cell (DSSC), by using density-functional molecular dynamics simulations at room temperature. Our results show that H$_2$O does not dive into the unbound Ti$_{5C}$ sites on the (101) surface kinetically, once the coverage of MeCN is saturated ($\Theta \sim 0.6$). On the other hand, H$_2$O adsorption through hydrogen bond with surface O$_{2C}$ sites, not a Ti$_{5C}$ site, is found the most stable if MeCN solvent is introduced to H$_2$O-preadsorbed TiO$_2$ anatase (101) surface (see Figure 1). This no-adsorption character of Ti$_{5C}$ site in the aprotic solvent MeCN is in stark contrast to the case where the (101) surface is immersed by H$_2$O layer or liquid H$_2$O. The adsorbed H$_2$O molecule via the hydrogen bond between O$_{2C}$ and H$_W$ has its $1b_1$ orbital at an energy just below the valence band maximum of TiO$_2$. Therefore, this H$_2$O has a sufficient possibility to become a cation radical by capturing hole generated by irradiation, which may attack the dye molecules towards the desorption. We thus demonstrate that removing H$_2$O from the anatase (101) surface prior to introduction of the MeCN electrolyte solution is crucial to make the DSSCs more durable and efficient.

First-principles study on structural and electronic properties of Pd(dmit)$_2$ salts under high pressure

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A series of metal dithiolene compounds $\beta'$-type (Cation)[Pd(dmit)$_2$]$_2$ (Cation= Me$_{x}$Et$_{5}$A, x = 0, 1, 2, A= P, As, Sb; Me=CH$_3$, Et=C$_2$H$_5$, dmit = 1,3-dithiol-2-thione-4,5-dithiolate) exhibit a variety of electric and magnetic properties such as pressure induced superconductivity, valence bond solid state and quantum spin liquid state. Most of $\beta'$-Pd(dmit)$_2$ compounds are Mott insulators at ambient pressure associated with a relatively narrow and half-filled conduction band. [1, 2] Previous theoretical and experimental studies for these compounds share the following common features; 1) Pd(dmit)$_2$ unit is strongly dimerized with one negative charge [Pd(dmit)$_2$]$^2^-$.

Conduction bands crossing at the Fermi level are mainly composed of the antibonding HOMO of Pd(dmit)$_2$ dimer. The half-filled bands originate from the strongly dimerized nature of the Pd(dmit)$_2$ molecules. 2) The electronic structure of the anti-bonding HOMO bands represents two-dimensional quasi triangular networks in terms of the Pd(dmit)$_2$ dimers. The anisotropy of the triangular lattices is slightly different from one to another Pd(dmit)$_2$ salt depending on the type of the counter cation. Therefore, pressure effects on electric properties of $\beta'$-type Pd(dmit)$_2$ salts with many kinds of cations have been extensively investigated, and a rich variety of electric properties was reported. For example, Me$_4$Sb and Et$_2$Me$_2$P salts exhibit pressure-induced superconductivity around 1GPa, but these salts shows non-metallic behavior again under higher-pressure. [3] On the other hand, Me$_4$P and Me$_4$As salts have never exhibited a metallic behavior under hydrostatic pressure up to 8GPa. Quite recently, the four-probe electrical resistivity for Me$_4$P and Et$_2$Me$_2$P salts has been measured up to 20GPa by using a diamond anvil cell. [4] The results clearly show that a metallic state appears at greater than 10GPa and 13.6GPa, respectively. It is also noted that these new metallic phases disappeared when higher-pressure is applied. In the present study, electronic structures of Me$_4$P and Et$_2$Me$_2$P salts at extremely high pressures are investigated using first-principles calculations based on the density functional theory. Structural optimizations for lattice parameters and internal coordinates under hydrostatic pressure up to 20GPa are performed theoretically using the ultra-soft pseudo-potential method with the generalized gradient approximation. We focused on how the crystal structures are changed by hydrostatic pressures, and demonstrate that many bands overlap with the antibonding HOMO bands near the Fermi level. The possible origins of the phase transitions will be also discussed.

Unconventionality of High-\(T_c\) Superconductivity in Layered Nitrides MNCl (M=Ti, Zr, Hf):
A Study based on Density-Functional Theory for Superconductivity

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Layered-metallonitride-halide superconductors [1] have been attracting much interest due to its superconductivity induced by electron doping with high critical temperature \(T_c\) up to 26 K. The pairing mechanism is yet to be clear; an \(s\)-wave gap is indicated from STM/STS [2], NMR [3], and specific-heat [4] measurements, while the isotope-effect coefficient of nitrogen is small [3]. Electron-phonon coupling is suggested to be small [4, 5], whereas they seem to belong to strong-coupling regime [2]. Clarification of the microscopic mechanism is highly desired.

The aim of the present study is to obtain microscopic insights into the mechanism of superconductivity in layered metallonitride halides from \textit{ab-initio} calculations. We have applied superconductivity density functional theory (SCDFT) [6] to the lithium-doped chlorides \(\beta\)-MNCl (M = Ti, Zr, Hf). The SCDFT has an advantage that it can treat the electron-phonon coupling and electron-electron interactions on the equal footing. It is widely known that the SCDFT accurately reproduces the critical temperature \(T_c\) of the conventional BCS superconductors [7]. However, our results show that the SCDFT for \(\beta\)-MNCl substantially (50\%) underestimates the experimental \(T_c\). In addition, we have found that the \(T_c\) increases as the doping rate increases, being an opposite tendency with the experiments [8]. These discrepancies strongly suggest that the \(\beta\)-MNCl is not a conventional BCS superconductor and imply the existence of a mechanism different from the electron-phonon coupling. We also predict that the lithium-doped \(\beta\)-TiNCl does not exhibit superconductivity down to 0.01 K. In this talk, we will show detailed results including electron-phonon coupling and electron-electron interactions, together with computational details for solving the gap equation in the SCDFT.

**First principle calculations of Pressure driven Insulator to Metal Transition in SrMnSb$_2$**

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RMnSb$_2$ system (R = Alkali Earth Metal) is analyzed by first principle DFT calculation using full potential linearized augmented plane wave method while PBE-GGA is used to account for the Exchange-Correlation potential. SrMnSb$_2$ has zig-zag chains of Sb ions while BaMnSb$_2$ has square planes of it. The results for SrMnSb$_2$ are consistent with the experimental observations and the electronic structures of these suggest the origin of this phase transformation in the relative size of the cation. Manganese layer is the main contributor near Fermi level. The application of pressure on SrMnSb$_2$ leads to a phase transformation from chain like semi-metal phase to BaMnSb$_2$ like Square planner structure showing metallic properties. A similar chain to square transition is also calculated for BaMnSb$_2$ accompanying an Insulator to Metal transition.
Bias Dependent Switching Rate of STM-Induced Melamine/Cu(001) Switch

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The manipulation or stimulation of molecules using Scanning Tunneling Microscopy (STM) is highly promising. Pan et al [1] found a STM-induced melamine/Cu(001) switch (C1 to C2, Figure 1) and analyzed its mechanism by a typical model. Such a model uses ad hoc parameters and the switching mechanism is not fully understood. The validation of them using first-principles calculations is required.

Current-induced forces are calculated by SMEAGOL program code [2], which is based on the nonequilibrium Green’s function method with density functional theory. The nudged elastic band (NEB) method was implemented into SMEAGOL to obtain minimum energy path (MEP) between C1 and C2 structures. Because the total energy of open systems is not well-defined, we calculated the potential energy by integrating forces along MEP.

The energy landscape calculated at zero bias was almost the same with that of Ref. 1. The energy barrier change was 0.06 eV within ±1.0 V, which is attributed to the dipole-filed interaction (no electron-wind force). Therefore, this barrier change can be reproduced by the calculation of a free molecule in electric field. (Figure 2) When the distance between the tip and the molecule is close, the barrier change becomes large but these configurations destroy the basic energy landscape. However, the barrier change of 0.06 eV is 1/4 smaller than the assumption in Ref. 1. The analysis of the switching mechanism by a master equation will be presented.

Electronic Structure and Magnetic Properties of Undoped Fe Pnictide Materials - LaFeAsO

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Beside the particular superconductivity, the electronic and magnetic properties of the parent material LaFeAsO have recently attracted more and more attentions in the field of material science. Several electronic structure calculations about LaFeAsO have been performed so far [1, 2, 3]. However, their conclusions are somehow inconsistent with each other because the results seem to depend on calculation schemes and types of the exchange-correlation functionals. More detailed calculation of this material is necessary to obtain full understanding of its electronic and magnetic structures. In this paper, we carefully studied LaFeAsO using the first-principles electronic structure calculation, Korringa–Kohn–Rostoker (KKR) Green's function method based on the generalized gradient approximation (GGA). The results show that the most stable magnetic state for LaFeAsO is the striped anti-ferromagnetic state with a Fe magnetic moment of 1.45 μB. In addition, we present our preliminary results by the fixed local spin moment method that could explain the difference between the experiments [4, 5] and calculations [6] up to now.

Photochemical reactions are fundamental, interesting, and complicated processes, because these drive structural changes and nonadiabatic transitions. Owing to the recent developments in laser technology, the dynamical photoinduced process including structural deformation, dissociation, isomerization, etc., have been investigated experimentally. To understand these excited-state dynamics theoretically, an accurate and efficient quantum simulation is required.

The simulation of photoinduced excited-state dynamics needs two ingredients. One is the nonadiabatic coupling terms (NACs) between the adiabatic states, and the other is the nuclear forces acting on atoms or ions on the adiabatic potential energy surfaces (APES) [1]. Recently, Hu et al. developed the efficient methods for calculating NACs using time-dependent density functional response theory [2]. However, the force calculation is still computationally expensive. In order to find a computationally reasonable force calculation method, we develop the excited-state force calculation method using the Casida ansatz [3]. This formulation is very simple, and the computational cost for the excited-state forces is almost the same as that of the NAC calculation.

First, we calculate the two APES for excited states of $^1\Sigma_u^-$ and $^1\Pi_g$ using adiabatic local density approximation for N$_2$ molecule. Comparing with the experimental value, the bond lengths of each state are well described within 0.03Å. Next, we calculate the excited-state forces using the Casida-ansatz formulation and compare it with the finite-difference numerical derivative of each energy curves. The Casida-ansatz force well reproduces the equilibrium bond length for $^1\Pi_g$ state, but overestimates that of $^1\Sigma_u^-$ by 0.1 Å. Thus, we consider that the forces on the APES with lower excited energies are well approximated by the Casida-ansatz force.

In the presentation, we discuss the difference in the force calculation method between the Casida-ansatz formulation and previous studies [4,5]. We discuss the Casida-ansatz forces for SiH$_2^+$ molecule as an example of open-shell molecule. We emphasize the usefulness of our technique by demonstrating the excited-state molecular dynamics simulation of the benzene molecule.

Thermal conductivity calculations of semiconductors from first-principles anharmonic lattice model

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Thermal conductivity is getting more and more important for manufacturing efficient micro-/nanostructured devices, especially for designing high-efficiency thermoelectric materials and heat-dissipating structures in CMOS transistors. From a theoretical point of view, a method for high-precision simulation is desirable to understand heat transport phenomena in these micro-/nanostructures.

For this purpose, we have proposed a new method for calculating lattice thermal conductivity of semiconductors which uses non-equilibrium molecular dynamics method and first-principles anharmonic lattice model (ALM) [1]. ALM employs a general function consisting of atomic displacements and harmonic, cubic and quartic force constants which are calculated from first-principles density functional theory. This method can be applied to complex systems with surfaces, interfaces and defects and no experimental data are needed.

We applied our method to silicon with various structures and obtained the lattice thermal conductivities (Fig.1). We estimated a bulk value with an extrapolation method \((L_z \to \infty)\) and obtained a reasonable value as compared to experimental results. We also calculated the lattice thermal conductivities with fixed boundaries where outermost atoms in the \(xy\) plane (which is perpendicular to the direction of the heat flow) were fixed. In these cases, thermal conductivity was about 10 times lower than the bulk values and the effect of surface scattering became larger in smaller cross-sectional area.

On the poster, we will present the details of our calculation settings and the analysis of surface scattering effects.

Electronic Structure Analysis of FKBP-ligands system based on FMO-LCMO

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In this study, we present our recent theoretical study on FK506 binding protein (FKBP) and some ligands complex systems by using fragment molecular orbital (FMO) calculation [1] combined with linear combination of molecular orbitals (LCMO), called as FMO-LCMO scheme [2]. Electronic structure between a ligand molecule and its environmental amino acids of FKBP is investigated.

In the FMO-LCMO scheme, we use fragment molecular orbital (FMO) method as an electronic structure calculation. In the FMO method, biomolecule is divided into fragments, then all fragments and their dimers (and optionally trimmers) are calculated under the electrostatic field generated by the environment. Finally total energy and density matrix is calculated with those of fragments. Then constructing Hamiltonian matrix of the whole systems as LCMO of each fragment from FMO calculations, we can obtain wave functions and orbital energies of the whole system. The following figure shows orbital energies and highest occupied molecular orbital (HOMO) of an FKBP-ligand system calculated by conventional first-principle calculation and our FMO-LCMO calculation, respectively.

The Role of $d$-Orbitals in Rashba-Type Spin-Splitting in Noble Metal Surfaces

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We investigate the Rashba-type spin-splitting in $sp$-derived Shockley surface states on (111) surfaces of noble metals, such as Au(111) and Ag(111), based on first-principles calculations including spin-orbit coupling. By turning on and off $l$-dependent spin-orbit coupling one by one, we find that although the surface states on Au(111) have predominantly $p$-orbital character, the spin-splitting in energy originates mainly from $d$-orbital character of the surface states. We also demonstrate that the spin splitting in surface states of both metallic surfaces can be controlled by varying the size of $d$-orbital parts of the surface-state wavefunctions. These results show that in addition to difference in the atomic spin-orbit strength in Au and Ag, difference in $d$-orbital contributions to the surface states makes substantial difference in the sizes of the Rashba-type spin-splitting in their surface electronic structures. This work was supported by the NRF of Korea (Grant Nos. 2009-0081204 and 2011-0018306), and computational resources have been provided by KISTI Supercomputing Center (Project No. KSC-2011-C3-05).
First-Principles Molecular Dynamics Study on Reaction Mechanisms of Nylon-6 Byproduct-Degradating Enzyme

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Nylon-6 is a long polymer generally consisting of more than one hundred units of 6-aminohexanoate (Ahx). During the production, the byproducts Ahx-linear and Ahx-cyclic oligomers represent wastes to be disposed. The Ahx-dimer hydrolase (NylB) has been found to be able to realize the degradation process. Recently, the enzymatic hydrolysis of the Ahx-linear dimer (Ald) into Ahx has been the target of increasing research efforts, with the purpose of developing an environmentally friendly way of disposing nylon wastes. However the detailed reaction mechanism is still an open issue. In this work, by using hybrid quantum mechanics/molecular mechanics (QM/MM), in combination with the metadynamics approach, we inspect the atomic-level mechanism occurring in NylB. The model system used was constructed based on the NylB X-ray structure (PDB accession code: 2ZMA). The QM region includes the catalytic site composed of Ser112, Lys115, Tyr170, and Tyr215, and the nearby amino acids, along with water molecules forming hydrogen-bonds with the active site.

Our calculations show that Ser-ÔγH attacks the amide compounds to generate a tetrahedral intermediates (Fig. 1), with a free energy barrier of about 0.7 eV.

We found that nucleophilicity of Ser112 is enhanced by the NH₃⁺ of Lys115 (Fig. 1a and b). During the conversion of the tetrahedral intermediate to the acyl-enzyme, Tyr215 donates H⁺ to the intermediate, breaking the N–C bond in Ald and releasing Ahx (Figs. 1b and c). At the same time, Tyr170 moves toward the bulk water. These results provide a first atomistic insight into the roles of catalytic amino acid residues, hence a hint to design and to improve practical applications.

Figure 1. Representative snapshots of the acylation reaction. The color code for atoms is cyan for C, red for O, blue for N, and white for H.
Development of First-Principles Maxwell+TDDFT Multi-Scale Simulator for Propagation of High-Intensity Laser Pulse

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Interaction between light and matter is described by the Schrödinger and Maxwell equations. For ordinary weak light wave, one can apply the perturbation theory for Schrödinger equation and decouple two equations with the dielectric function. However, for intense laser pulse, one cannot separate them because of the nonlinear electron response to the strong electric fields. So we must solve Schrödinger and Maxwell equations simultaneously.

Previously, we developed a framework in TDDFT to describe electron dynamics in bulk materials under spatial-uniform time-varying electric field solving time-dependent Kohn-Sham equation in real-time [1,2]. We now extend it to a first-principles simulator calculating the nonlinear electron dynamics and the propagation of electromagnetic field simultaneously.

Since the length-scale is much different between the laser wave length (μm) and the electron dynamics (nm), we employ two different spatial grids, expressing vector potential in the macroscopic grid and Kohn-Sham orbitals in the microscopic grids. We will show our calculation for the one dimensional propagation of electromagnetic field incident normally on bulk Si.

Figure 1

Figure 2

Figure 1: Behavior of reflected and transmitted waves when intense laser pulse (10^{14} W/cm^2) irradiates normally on the surface of bulk Si.
Figure 2: Reflectivity as a function of laser intensity.

First-principles calculations of mono-hydrogen and di-hydrogen in Graphene and Carbon Nanotubes

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Carbon Nanomaterials have attracted much attention since they are candidates for post-silicon materials. Since hydrogen is a common impurity in graphene [1-3] and carbon nanotubes (CNT), it is important to clarify how the hydrogen impurity affects the electronic structures of graphenes and carbon nanotubes. Also controlling impurity is important for new device materials.

Now we study mono-hydrogen in graphene, CNT (5,5) and CNT (10,0). We perform spin-polarized generalized gradient approximation by using first-principles calculations. In the most stable structure of mono-hydrogen, the hydrogen atom is bonded to one of the carbon atoms in the graphene sheet [Fig. 1(a)] and also hydrogen atoms are located on the outer sides of CNT (5,5) [Fig. 1(b)] and CNT (10,0) [Fig. 1(c)]. The bond lengths between the hydrogen atom and the nearest neighbor carbon atom are 1.14 Å, 1.12 Å and 1.12 Å for graphene, CNT (5,5) and CNT (10,0), respectively. These bond lengths are close to that of the CH\textsubscript{4} molecule (1.09 Å), which is typical for sp\textsuperscript{3} C-H bond lengths. In these three cases [Fig. 1] the spin polarized states are found to be the most stable and the magnetic moments are 1 \( \mu_B \).

![Fig. 1. Spin densities of the mono-hydrogen in the graphene, CNT (5,5) and CNT (10,0).](image)

In the most stable structure of the di-hydrogen in the graphene, each of the two hydrogen atoms are bonded to host carbon atoms, which are the nearest neighbor and the two hydrogen atoms are located on the opposite sides. On the other hand, in the most stable structure of the di-hydrogen in the armchair edges (5,5) and zigzag edges (10,0) carbon nanotubes are located on the outer side. The electronic structures of the above most stable geometries are nonmagnetic. However, when the two hydrogen atoms are bonded to the same sublattices of the host materials, the electronic structure is spin-polarized. The magnetic moments are found to be 2 \( \mu_B \).

References:
Fermi surface and spin texture of the noncentrosymmetric superconductors Li$_2$Pd$_3$B and Li$_2$Pt$_3$B

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Effect of spin-orbit coupling (SOC) associated with broken inversion symmetry has been a central issue in condensed-matter physics. Regarding the superconductivity, lack of inversion center implies that the pairing state is no more classified by the parity and is in general given by the admixture of spin-singlet and spin-triplet pairs. Li$_2$Pd$_3$B and Li$_2$Pt$_3$B crystallize in the same noncentrosymmetric cubic structure (space group P4$_3$32) while their superconducting nature is completely dissimilar. Nuclear magnetic resonance [1,2] and some other experiments indicate that Li$_2$Pd$_3$B ($T_c=7$K) is a fully-gapped spin-singlet superconductor while Li$_2$Pt$_3$B ($T_c=2.7$K) has line nodes in the order parameter and has considerable spin-triplet component. To clarify the fundamental electronic structure of these compounds, we investigate Fermi surface (FS) and spin texture $S(k)=\langle \Psi_k | \sigma | \Psi_k \rangle$ by means of the density-functional first-principles calculation. We adopt all-electron FLAPW method and GGA. The effect of SOC on FS is more dramatic in Li$_2$Pt$_3$B, reflecting the fact that ($Z_{Pt}/Z_{Pd}$)$^2\sim3$ and Li$_2$Pt$_3$B has more $d$ weight at $E_F$. FS of Li$_2$Pd$_3$B throughout the whole Brillouin zone comes along with two sheets, which are identified to be spin-split pair (see Fig. 1). Calculated average of $|S(k)|_{FS}=0.95$ over FS reveals that the wave functions are roughly given by pure spin-up or down. In the case of Li$_2$Pt$_3$B, it is difficult to identify the spin-split partners and most parts of FS are made of single sheet. Calculated $|S(k)|$ highly deviates from 1: $|S|_{FS}=0.72$. We demonstrate that the interband SOC plays essential role in Li$_2$Pt$_3$B.

$\text{Li}_2\text{Pd}_3\text{B}$

$\text{Li}_2\text{Pt}_3\text{B}$

**Figure 1:** $k_z=0$ cross section of Fermi surface. Arrows represent $S(k)$.

Weak ferromagnetism in the lightly electron-doped CaMnO$_3$

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Perovskite Manganites show a variety of electronic and magnetic properties, such as colossal magnetoresistance, multiferroics, by the change of their physical environments through the temperature, chemical doping, and so on, and have much attentions due to their possibility as a functional material, as well as their fundamental importance. Among them, CaMnO$_3$ is the G-type antiferromagnetic (G-AFM) insulator in the low temperature, and its electronic and magnetic structure is efficiently changed by the electron doping. The electron doping is realized by the substitution of the Ca$^{2+}$ by the tri-, or quadri-valent ions, or O-site vacancies. As the result, the Mn$^{4+}$($d^3$) is partly replaced by the Mn$^{3+}$($d^4$) in a simple view. In experiments, regardless the type of the electron doping, the weak ferromagnetic (FM) component is detected in lightly electron doped regions [1-3]. The origin of this weak FM has been studied so far with the double exchange model, and two scenarios are proposed. One is the spin-canting in the G-AFM [4], and another is the AFM-FM phase separation [5].

In this study, we will clarify the origin of the FM component by means of the non-collinear spin density functional theory, including spin-orbit (SO) interaction. We will show that the canted G-AFM is stabilized by the electron doping, and the large segment of the FM component observed in the Ce-doped CaMnO$_3$ is explained by this spin-canting. Also, FM state is not stabilized at lightly doped regions, and the strong concentration of the doped electron is required for the phase separation.

The practical calculation is performed by using the QMAS code [6], in that the projector augmented-wave (PAW) method with plane wave basis is applied. The non-collinear magnetism and the SO interaction are treated by solving the fully relativistic version of the Kohn-Sham equation [7].

First-principles study of the orbital state in antiferromagnetic FeO

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Transition-metal monoxides MO(M=Mn, Fe, Co, Ni) have the rock-salt structure, and show the type-II antiferromagnetic ordering. Among them, FeO shows lattice distortion elongated along the spin-modulation direction [111] below the Néel temperature. The experimentally observed magnetic moment of FeO orients to [111] and amounts to 4.2μB, indicating a significant contribution from the orbital component. Thus, in FeO, the lattice, spin and orbital (t²g↓) degrees of freedom are considered to be strongly coupled, and its theoretical description is still challenging. Though some recent works have addressed the insulating property of FeO [1,2], the importance of spin-orbit coupling (SOC) is not well recognized. There were elaborated works based on the density-functional theory (DFT) with SOC [3,4]. However, the microscopic origin of lattice distortion and magnetic anisotropy energy (MAE) are not well discussed yet. Following the last presentation [5], we investigate the electronic structure, MAE, and the lattice distortion of FeO from first principles based on DFT and all-electron FLAPW method. We adopt the local density approximation (LDA) and LDA+U method. In the cubic phase (no distortion), when we assume [111] magnetization, we obtain two self-consistent solutions by LDA+U. The first one is a state corresponding to that in Ref. [1,2], in which the 3d electrons occupy the a1g band of the minority spin. The second one is a state in which the 3d electrons are accommodated in a sub-band of the e′g representation with the minority spin and has lower total energy. To examine MAE, we adopt the constrained local-moment technique [6,7] for several directions. We find that [111] is the easy magnetization axis and also that once the spin is tilted from [111] the a1g solution disappears and merges into the e′g branch. We further examine the effect of trigonal strain. Detailed energetics will be presented.

DFT-based First Principle Study of the Carrier Compensation Mechanism in Nb-doped Rutile TiO₂

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Despite its importance in electronic devices, prediction of the electron trapping character at an oxygen vacancy in a transition metal oxide is still a controversial issue in the field of computational material science. Using a DFT-band structure method at GGA+U level of the theory, we investigated the electron trapping character of the dopant in Nb-doped rutile and anatase TiO₂.

In anatase structure Nb-doped TiO₂ (TNO) shows the high electronic conductivity and the high visible-light transparency. For this reason, TNO is considered to be one of the most promising alternative transparent conducting oxides (TCO), which will potentially substitute the conventional indium tin oxide (ITO). However, the same composition of the atoms in rutile structure does not show such a prominent conducting feature. Recently, Deak et al. reported a DFT-based band structure calculation of Nb-doped TiO₂ in both polymorphs using the HSE hybrid functional. However, a careful convergence check is missing in their research.

We carefully calibrated the +U parameters for all three kinds of atomic species in the system. The +U(O 2p) was quoted from a recent work by Watson et al., and the +U(Ti 3d) and +U(W 4d) were determined as to satisfy the generalized Koopman’s theorem (gKT). The PBE functional was utilized. The Bader charge analysis was carried out to see the charge distribution of the trapped electron. Two (Three) sizes of the periodic unit cell were employed in order to see the cell-size dependence in anatase (rutile). The number of atom is 48 in the smallest unit-cell, and 96 in the largest.

Our calculation revealed the electron calculated with use of spin-restricted method is not actually trapped at the Nb dopant atom, although the population is the highest there. The trapping is observed only for spin-unrestricted calculation, and the electron was trapped at two Ti atoms adjacent to the Nb atom along the [001] direction. This result is substantially different from the report of Deak et al. In addition, the formation energy of Nb⁵⁺ + e⁻ and Nb⁴⁺ were very close to each other when the Fermi level is at the conduction band minimum (e_F = e_CBM). This finding also indicates the subtlety character of the charge trapping, and the necessities for the proper determination of the +U parameters.

References
A numerical method has been developed [1] to calculate the Hartree-Fock-type orbital-dependent exchange energy and potential at a computational cost that scales as order-$N$ with respect to the size of the system. The order-$N$ scaling is achieved by approximating the long-range region of the exchange (Fermi) hole with a parameterized model function and, therefore, by being possible to terminate the numerical integration in real-space at a certain radius. The self-consistent determination of the model parameters by enforcing moment-matching conditions ensures that the exchange potential correctly approaches $1/r$ as the distance from the nucleus $r$ increases. The accuracy and speed of the computation depends on the shape and declination rate of the screening function that is multiplied to the exchange hole in order to separate the long-range portion from the remaining portion of the exchange hole. In our numerical test for the noble-gas atoms, the Gauss’s error function (erfc) was employed as the screening function and the declining rate $\mu$ was varied from $\mu = 0.1/$Bohr to $\mu = 0.5/$Bohr. The result shows that the error in the total energy is similar to that of the optimized effective potential method when $\mu = 0.3/$Bohr is used. The error in the eigenvalue of the highest occupied state is less than 1% for all the values of $\mu$. Since the state has a more extended wave function than the other lower states, this indicates the successful reproduction of the correct $1/r$ asymptotic tail of the exchange potential.

Long-range corrected meta-generalized gradient approximation density functional with dispersion corrections

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By applying a general scheme for systematically modeling long-range corrected (LC) hybrid density functionals \cite{1} to the form of hybrid meta exchange-correlation functional M05 \cite{2}, and including empirical atom-atom dispersion corrections, we present a new LC meta-generalized gradient approximation (meta-GGA), called $\omega$M05-D, for thermochemistry, kinetics, and noncovalent interactions.

$\omega$M05-D is parameterized against 412 data points: 18 atomic energies, the G3/99 main-group atomization energy database, 40 ionization potentials (IP), 25 electron affinities (EA), and 8 proton affinities (PA) of the G2-1 set, the 76 barrier heights of the NHTBH38/04 and HTBH38/04 sets, and the 22 noncovalent interactions of the S22 set. Comparing to $\omega$B97X-D \cite{3} on some important properties of training sets, $\omega$M05-D performs better result for atomization energies, and slightly inadequate results for IP and noncovalent interactions.

However, good performance in test sets makes up deficient that in training sets. For noncovalent interactions of CT7/04, DI6/04, WI7/04 databases and nine data taken from JSCH2005 database, $\omega$M05-D provides improvement over M05-2X \cite{4} and $\omega$B97X-D. $\omega$M05-D also possesses smaller self-interaction errors than M05-2X and $\omega$B97X-D, so that represents the best performance in dissociation of symmetric radical cations and application of time-dependent density functional theory (TDDFT), such as Rydberg excitations and long-range charge transfer (CT) excitations. Another advantages relative to LC hybrid functionals are accurate highest occupied molecular orbital (HOMO) energies and lowest unoccupied molecular orbital (LUMO) energies. For G58 and IP138 sets, we calculate band gaps by the difference between HOMO and LUMO energies and IP by HOMO energy, and then obtain the best result performed by $\omega$M05-D.

\begin{thebibliography}{9}
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Actinide elements and compounds produce a plenty of interesting physical properties, not only of their nuclearity but also of the magnetism and electronic, due to the $5f$ states of actinide elements. PuO$_2$ is considered as an important component of cycling Mixed OXide (MOX) for nuclear reactor fuel.

Many theorists have investigated structural, thermodynamic, and electronic properties of plutonium oxides by first principles. Jomard et al. provided a practical procedure which compares the energies of all energy minima of Occupation Matrixes (OM) and determines the ground state.[1] However, the occupation matrix of the minimum energy was not provided and the Spin-Orbital Coupling (SOC) was not taken into account. This work is engaged in the ground state properties of PuO$_2$ with OM method under SOC.

The ground state of $\delta$-Pu was investigated with SOC applying GGA+U. The electron number and orbital magnetic moment (MM) are good with the experimental data whereas the spin MM is a little lower. This intermediate coupling between $LS$ and $jj$ in $\delta$-Pu is extended to PuO$_2$ though the analysis on relativistic states $f_{5/2}$ and $f_{7/2}$. In order to find the ground state, all electronic configurations with different initial OM were calculated to identify the equilibrium state. Then the structural and electronic properties were discussed. Jahn-Teller distortion was checked.

Effect of messenger on small protonated water cluster

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Water is one of important substance in earth, and H+(H2O)n cluster has been extensively studied as a microscopic model to investigate the hydrogen bonding network of protonated water cluster.¹ The messenger mediated spectroscopy is a widely-used technique to study gas phase ionic species. It has been thought that proton transfer is an interconversion of two motifs, “Eigen” (H3O+ or H3O+(H2O)3) and “Zundel”. (H5O2+ or H2O…H+…OH2).² In this study, we use various DFs such as LSDA, GGAs, hybrid GGAs, meta-GGAs, long-range exchange GGAs, and double hybrid GGAs to calculate the interaction energy between clusters and messenger, where the geometries of clusters are directly frozen from optimization results of cluster and messenger.

In order to estimate the accuracy of our benchmark data, we compare those DFs with more accurate estimates of CCSD(T)/CBS(aT-aQ) level of theory. The counterpoise correction was employed in all energy calculation to minimize the effects of basis set superposition error (BSSE). Potential energy curves along the messenger dissociation coordinate are examined both by more accurate reference CCSD(T)/CBS and those density functional mentioned above. Although most DFT calculation are underestimated the interaction energy between protonated water cluster and messenger, the results with wB97X³ and wB97X-2(LP) functional are the most close to the CCSD(T)/CBS results.


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A First Principles Calculation on Graphene-based Heterojunctions

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Graphene, which consists of a single atom-thick plane of carbon atoms arranged in a honeycomb lattice, has attracted a significant amount of research interest because of its novel electronic, mechanical, and thermal properties arising from its unique 2D energy dispersion. Recently, it becomes an important issue to investigate the properties of heterojunction graphene-based devices.

In this research, we investigate the electronic structures for several heterojunctions including graphene, graphene oxide and graphane (fully-hydrogenized graphene). In addition, the interface charge transfer behavior of metal and these nanocarbon materials is also investigated. Electron density difference calculations were used to evaluate the charge transfer behavior. Band structures, potential and orbital calculations were used to build the band alignment diagrams. Our result provides an insight for the experimentally observation in the graphene-based heterojunction devices.

**Ab initio** Derivation of Low-energy Models for Aromatic and C$_{60}$ Superconductors

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Recent discovery of superconductivity in aromatic compounds (ex. alkali-doped picene) [1] and in fcc/A15 Cs$_3$C$_{60}$ under pressure [2] has stimulated a renewed interest in molecular superconductors such as K$_3$C$_{60}$ and Rb$_3$C$_{60}$ [3]. To clarify the mechanism of the superconductivity, it is essential to understand low-energy electronic structure of these systems.

In the present study, we derive ab initio extended Hubbard models using maximally localized Wannier orbitals [4] to establish a firm starting point for studies on the low-energy properties of these systems. The transfer integrals were calculated as matrix elements of the Kohn-Sham Hamiltonian. The Wannier matrix elements of screened Coulomb/exchange interactions were derived with the constrained random phase approximation [5]. We found that electronic-correlation strength has a positive correlation with superconducting transition temperature $T_c$ in C$_{60}$ compounds (left), while it gives an opposite trend for aromatic compounds (right). We will report the details of calculation, parameters of effective models, and the relation between electronic correlations and superconductivity.

![Figure](image)

Figure (Left) Relation between correlation strength and superconducting and magnetic transition temperature in fcc A$_3$C$_{60}$ (A=K,Rb,Cs). (Right) Relation between correlation strength and superconducting transition temperature in aromatic compounds.

Recent progress in a linear-scaling DFT code CONQUEST: parallel efficiency and optimisation of local orbitals

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CONQUEST is a linear-scaling (or O(N)) DFT\textsuperscript{[1]} code developed jointly by UCL and NIMS. It is very efficient on massively parallel computers and we have recently shown a possibility of DFT calculations on million-atom systems using the code\textsuperscript{[2]}. With these abilities, CONQUEST has been applied to several kinds of systems, like Ge nano islands on Si(001) \textsuperscript{[3]}, DNA and some other biological systems.

In this talk, we will present two recent topics in the development of the code. First, we will report the improvement of its parallel efficiency. So far, CONQUEST has used flat MPI parallelisation and the performance of the weak scaling is already close to ideal. However, in order to decrease the wall time for one SCF or MD step, the efficiency of the strong parallel scaling is also important. For this purpose, we have recently introduced OpenMP parallelisation in the part of sparse matrix multiplications, which is the most expensive part in the code. Such hybrid (OpenMP+MPI) parallelisation is important also for the use of supercomputer K. We will show the performance of the code on different platforms and demonstrate that the code is ready for MD or structure optimisation of huge systems.

The second topic is about the accuracy and efficiency in the optimisation of the local orbitals. CONQUEST minimizes DFT total energy with respect to a density matrix, instead of solving eigen functions of Kohn-Sham equations. The density matrix is expressed by local orbitals called support functions, and the accuracy of the calculations depends on the quality of the local orbitals. To achieve the high accuracy with the CONQUEST code, we optimise the local orbitals expressed by local basis set functions. Here, we will report the accuracy of the method when we use pseudo atomic orbitals (PAOs) as a basis set. Comparison with the results using B spline (called blips) basis sets, and comparison with other codes will be presented. The improvement in the optimisation of PAO coefficients will be also discussed.

Methanethiol on noble metal surfaces: Determination of reaction paths

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Adsorption and reaction of methanethiol (CH$_3$SH) on transition metal surfaces have extensively been investigated during the last decades. Reactions on noble metal surfaces have drawn particular attention because of their connection to self-assembled monolayers [1]. A large number of computational studies were reported on adsorption states (e.g. adsorption sites and binding energies) of thiol (CH$_3$SH) as well as thiolate radical (CH$_3$S), and a solid understanding on their adsorptions has been established. On the other hand, determination of the reaction pathways in these systems did not appeared until recently [2].

We present a density-functional study on reaction paths of methanethiol on (111) surfaces of noble metals using plane-wave basis sets. The metal substrate is represented by a four-layer slab, where each layer involves 12 metal atoms. Adsorption states where methanethiol is (1): molecularly bonded to the surface and (2): dissociated into methanethiolate and hydrogen on the surface are identified using the PBE exchange-correlation functional. The nudged elastic band (NEB) scheme is employed for determining reaction pathways. The comparison of the reaction paths between different metal substrates will also be presented.

First-Principles Study of Various SiC polytypes

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We calculated the electronic and lattice properties of 2H-, 3C- (= 3H-), 4H-, 5H-, 6H-, 8H-, 10H-, 12H-, and 18H-SiC polytypes which are sp3-bonded compounds[1][2]. A tetrahedral structure is formed by Si and C atoms in their hexagonal polytypes whose possible symmetries are P6\textsubscript{3}mc and P3\textsubscript{1}m. Numbers of possible polytype structures are 1 for 2H - 5H, 2 for 6H, 6 for 8H, 18 for 10H, 58 for 12H, and 2435 for 18H[3]. We investigated all possible structures of 2H - 8H, six structures of 10H, seven structures of 12H, and one structure of 18H. Calculated hexagonalities (H) are 0 %, 16.7 %, 20 %, 25 %, 33.3 %, 40 %, 44.4 %, 50 %, 60 %, 66.7 %, 75 %, 80 %, 83.3 %, and 100%. Hexagonality is a ratio of the number of a hexagonal (h) character and total number of cubic (c) and h characters in a unit cell. 44.4% is hexagonality of one polytype structure in 18H-SiC. We calculated their electronic properties (electronic band structures, band gap values, valence band maximum (VBM), and conduction band minimum (CBM)). All calculated electronic band structures are non-metallic and band gaps are indirect. Lattice properties (lattice constants and internal coordinates of atoms in the unit cell) were optimized by the total energy pseudopotential method based on the local density approximation (LDA[4]) and the generalized gradient approximation (GGA[5]). There is no clear trend in the order of the total energies for the SiC polytype structures. The total energies of three 10H-SiC polytype structures by LDA and GGA are slightly lower than that of 4H-SiC. One of them, whose stacking sequence is ABCACBCACB (ABC notation) and H = 40 %, is lower by 2.4 meV/Si2C2 (LDA) and 3.1 meV/Si2C2 (GGA) than 4H-SiC and lowest in the calculated SiC polytype structures. The Zhdanov notation of 10H-SiC(ABCACBCACB) is “3322”.

Interaction energy and large-scale DFT calculations of DNA with unnatural base pair systems

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We present our recent theoretical study on DNA with unnatural base pair, called Ds-Pa, systems using two different methods. First we investigated the intermolecular interactions of the unnatural base pair Ds-Pa in the gas phase by LDA, GGA and HF-MP2 using the Gaussian code. We have calculated the potential energy surface analysis as a function of the distance between the two molecules. Differently from hydrogen bond formation in the natural A-T or G-C Watson-Crick base pairs, we have found that the interaction between Ds and Pa molecules is very weak and mainly governed by the dispersion forces. This result suggests that the stabilization of unnatural base pair within DNA double helix structure, which is observed in experiments, should depend on the environment such as the frame spacing of DNA backbone, the interaction for its upper and lower base pairs, and/or the existence of solvent.

Based on these results, we have applied the CONQUEST code to a hydrated DNA system including one unnatural base pair, whose structure is shown in the right figure. In this talk, we show the preliminary data of our linear-scaling DFT calculations on such a complex system. The system consists of 11,912 atoms (763 atoms for a DNA including one unnatural base pair, 22 Na counter ions and 3,709 water molecules). Our linear scaling DFT methodology is robust and accurate in biomolecular systems, for example, the SCF calculation is very stable and a rapid convergence over 10,000 atoms (44 hours/512 cores) on NIMS supercomputer. As in our previous study on hydrated (natural) DNA system, we have compared the atomic forces and the total energies calculated by CONQUEST with those by AMBER. We have found that the atomic forces for unnatural base pair part, whose force field is newly made by us, show reasonable agreements.

Origin of the $n$-type Transport Behavior of C$_{59}$N Encapsulated Semiconducting Single-Walled Carbon Nanotube

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Following the discovery of single-walled carbon nanotubes (SWCNTs) two decades ago [1], many new hybrid materials with novel electronic properties, such as C$_{60}$ molecule encapsulated in SWCNTs namely “carbon peapod” [2], are synthesized. Recently, many researchers are widely interested in the C$_{59}$N azafullerene encapsulated into semiconducting SWCNTS (C$_{59}$N peapod) that shows the $n$-type transport characteristics [3]. This result is in sharp contrast to the typical $p$-type characteristics of pristine semiconducting SWCNTS, and C$_{60}$ encapsulated semiconducting SWCNTs. However, the origin of the $n$-type characteristics of C$_{59}$N peapod is still unclear: It may be caused by the charge transfer between azafullerenes and SWCNTS [3], or by the different preparation methods [4]. In this work, we unravel the origin of $n$-type transport behavior of C$_{59}$N peapod based on first-principles electronic structure calculations [5].

All calculations were performed using the local density approximation (LDA) in the framework of density functional theory (STATE code). Ultrasoft pseudopotentials were used to describe the electron-ion interaction, in which the valence wave functions and charge density were expanded in terms of a plane-wave basis set with cutoff energies of 25 and 225 Ry, respectively. The C$_{59}$N peapod was simulated by using a (17,0) semiconducting SWCNT containing a chain of C$_{59}$N molecules. Electronic structure of C$_{59}$N peapod under electric field was investigated by using the effective screening medium (ESM) method [6].

We find that the unique $n$-type behavior of C$_{59}$N peapod originates from the monomer form of C$_{59}$N molecule encapsulated in SWCNTS. The singly occupied (SO) state of C$_{59}$N lies in the energy gap of the SWCNT. Under the doping electron process (via electric field), the energy of this SO state shifts monotonically upward and finally crosses the bottom of the conduction band of the carbon nanotube. Because of this shift to higher energy, the SO state acts as a shallow donor state for the conduction band of the carbon nanotube, which leads to the $n$-type transport behavior of C$_{59}$N peapod.

Electronic structure and magnetic properties of YMn$_2$

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YMn$_2$ is an interesting material from the view point of magnetism. It transforms from a paramagnetic to an antiferromagnetic phase at 100 K. A giant magneto-volume expansion of 5% accompanies the transition. This transition, however, disappears by substitution of Sc for Y by 3%. Experimentally, the magnetic structure in the antiferromagnetic phase is thought helical with a long period based on a [001]-antiferromagnetic structure[1]. First-principles calculation for these materials, especially for doped cases, is important in order to discuss the behavior of the antiferromagnetism and the associated large magneto-volume effects. In fact, several first-principles calculations have been performed so far for this system. However, those first-principles calculations seem to involve several problems. For example, contrary to the experimental observations, the calculations concluded that the most stable magnetic structure was a [000]-antiferromagnetic structure[2].

To clarify the origin of the discrepancy between the experiments and theories, we performed detailed first-principles electronic structure calculations using various different potential-models and different exchange-correlation potentials. For the former, we tested the atomic sphere approximation and the muffin-tin potential model. For the latter, we examined the local density approximation (LDA) and the generalized gradient approximation (GGA). In case that other metastable states different from those obtained by self-consist determinations of the electronic structure exist, we also calculated the binding surfaces of YMn$_2$ with respect to the lattice constant and sub-lattice magnetization of the Mn as two independent variables. Both the [000]- and [001]-structures were considered. For these calculations, an extension of the fixed spin-moment method to the one for a sub-lattice magnetization, i.e., fixed local spin moment method, was developed.

We found that the results were rather sensitive to the approximation of the exchange-correlation energy. The influence of the choice of the potential model seems to be of secondary importance. All the combinations of the different potential models and the approximations to the exchange-correlation energy failed to explain the experimental observation in any consistent way. Thus, we concluded that the improvement of the treatment of the exchange-correlation energy should be essential for a reasonable description of the system.

Spin-Polarized Electronic States and Rashba Effect in the Graphene on Ni(111)

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Graphene, a two-dimensional honeycomb lattice consisting of C atoms, shows useful properties for spintronics applications. Recently, spin-split electronic states in the graphene on Ni(111) is discussed extensively [1-3].

By using noncollinear spin-density functional theory implemented in openmx code[4], we predict spin-polarized electronic states of the graphene on Ni(111) in real- and momentum-space. The Dirac-cone shaped band structure was broken by strong hybridization between monolayer graphene and substrate Ni(111).

On the other hand in the bilayer graphene on Ni(111), the Dirac-cone shaped band recover only in minority spin. The relativistic spin-orbit effect make non-collinear spin vortex (Rashba Effect) in the momentum space. This spin noncollinearity in momentum space may make significant effects on the electrical transport properties of the graphene/Ni(111).

Protonated carboxyl anchor for stable adsorption of N749 Ru dye (black dye) on TiO$_2$ anatase (101) surface

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We investigate the adsorption stability of N749 Ruthenium dye (RuL(NCS)$_3$, L=4,4’,4’’-tricarboxy-2,2’:6’,2’’-terpyridine: black dye (BD)), a most efficient dye for dye-sensitized solar cell (DSC), via protonated and deprotonated carboxyl group anchors on TiO$_2$ anatase (101) surface, by density functional theory (DFT) based geometry optimization with supercell. Among configurations with one and two carboxyl anchors, the BD adsorption anchored with one protonated carboxyl group is found the most stable, in contrast to the previous reports that examine Ru dyes with deprotonated anchors for the stable adsorption structures on the TiO$_2$ surfaces. It is shown that the proton retained in BD and the two-fold coordinated oxygen (O$_{2c}$) on the surface form a hydrogen bond, which accounts for the stability of the protonated carboxyl anchor. The stability of one anchor is attributed to the rigid character of terpyridine in BD. In order to verify the stability of this protonated anchor, we calculate UV-visible spectra of representative optimized structures of adsorbed BD by time-dependent DFT with the cluster boundary condition, and compare to the relevant experimental data. The relative positions of experimental peaks and tails are found most consistent with the adsorption via one protonated carboxyl anchor, the most stable form in this study, than the structures with deprotonated anchors. We also calculate the electronic density of states of some optimized configurations of the whole system, and confirm that the proton position largely affects the electronic states. Thus, this novel way of adsorption via protonated carboxyl anchor may give a new perspective for the efficiency improvement of DSCs.
Unlike the typical iron-pnictide superconductors, the iron-chalcogenide superconductor has neutrally charged layers without intervening ion spacers or charge-reservoir layers. Using the first-principles density function theory (DFT) calculations including non-local functional, we have clarified that the weak interlayer interaction in FeSe is mainly induced by weak van der Waals (vdW) force. Conventional DFT calculations based on the local density approximation (LDA) or the generalized gradient approximation (GGA) fail to explain structural properties of FeSe, while they are successful in other iron-pnictide superconductors. When the non-local functional is included with the GGA+NL method, the calculated lattice constant and the pressure effect of FeSe become consistent with the experimental results. The binding energy of a FeSe layer is 0.16 eV/layer, which is an order of magnitude smaller than that of other pnictide layers with ionic bonding. The present work reveals that, in the description of structural and superconducting properties of FeSe, the vdW interaction should be considered as an interlayer bonding mechanism.
Ab-initio study of the capacitance density of high-k nanocapacitors

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The dimensions of capacitors in dynamic random access memory (DRAM) cells are shrinking continuously to realize higher packing density and larger memory capacity. As the area per capacitor decreases, higher capacitance density becomes necessary for reliable operation. To this end, high-k dielectrics such as TiO₂ and SrTiO₃ (STO) are being considered for next generation DRAM capacitors. However, experimental works have shown that high-k/metal interfaces often suffer from degraded dielectric properties [1]. Contamination, defects, and the intrinsic dead layer effect [2] are possible factors contributing to such degradation, although it is not entirely clear how much each factor influences the total capacitance. In this work, we employ first principles simulation and our newly developed orbital separation approach [3] to calculate the capacitance of nano-sized capacitors utilizing high-k dielectrics to examine the limit in capacitance density.

Figure 1 shows the calculated dependence of the inverse capacitance of SrRuO₃(SRO)/STO/SRO system on the STO film thickness at 0.05 V. The interface of this model is perfectly epitaxial without any defects. Classically, the inverse capacitance is proportional to the thickness, but our result shows that it converges to a certain value as the thickness is decreased. That is, scaling of the dielectric thickness below 3 nm does not seem to result in higher capacitance density. This is rather thick and is almost within reach utilizing state-of-the-art fabrication techniques.

Computational Study on the Transport Properties of Rigidly Interconnected Carbon Nano Foam

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By applying the non-equilibrium Green function approach in combination with density-functional theory, we investigate the electronic transport properties of rigidly interconnected graphitic structures along a certain axis. We focus on artificial crystalline lattices including schwarzite, which is sp\textsuperscript{2} carbon minimal surface. Such lattices consist of core parts with locally negative Gaussian curvature, which are connected through interconnection parts of (4,4) carbon nanotube segments either one-dimensionally or three-dimensionally [1]. We calculate the electrical conductance of the core part comprised of (4,4) CNT-schwarzite-(4,4) CNT and explore the effects of different core connectivity and structural defects introduced near the core parts. Our results show that the core connectivity and the position of the defects play critical roles in electronic transport properties. We also study the dopped schwarzite system with intercalation of dopants at the center of core parts which may shift the Fermi level as compared with those of the bare system [1]. It is expected that the electronic transport properties can be adjusted by controlling the amount and sign of dopants in the system.

An experiment has demonstrated that hydrogen sulfide (H2S) can be selectively and sensitively by carbon nanotubes (CNTs) network devices functionalized with 2,2,6,6-Tetramethylpiperidin-1-yloxyl (TEMPO). The functionalized CNTs devices show significant conductance drop in the presence of H2S. Using the first-principles calculations, we investigate a sensing mechanism of such TEMPO-functionalized CNT devices for H2S. First, we explore the adsorption properties of TEMPO on both (10,0) and (5,5) CNTs, the first of which is semiconducting and the other metallic, and those of H2S on the functionalized CNTs. The electronic structures were calculated for all three cases (pristine CNTs, TEMPO-functionalized CNTs, and H2S on TEMPO-functionalized CNTs). Moreover, we consider an effect of O2 molecules, which naturally exist in any experimental environment. Finally, we use Green function approach to investigate the electrical transport properties of each case. We find the interaction between H2S and CNTs through TEMPO may block some conduction channels resulting in the conductance reduction.
Size and Lattice Effects of Plasmonic Properties of Na Spheres Investigated by Real-Time TDDFT Simulations

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Plasmonics has become a rather hot research focus recently due to its prospects in various applications of nano-technology, notwithstanding that plasmonic excitations have been an old topic in physics. In the classical limit, plasma can be described as a collective motion of nearly free electrons taking movements following Maxwell’s equations inside a metallic material with a fixed dielectric constant. However, quantum mechanics (QM) descriptions have been shown to be important for systems with subnanoscale couplings of plasmons – the quantized plasma [1, 2]. Thus, it is interesting to further investigate how the plasmonic properties are affected by, for example, system sizes as well as the positive background model in the subnanoscale regime.

In this report, we specifically study the optical absorption spectra and density oscillations of plasmons of various small size Na spherical structures with positive uniform background (jellium model) using QM-based time-dependent DFT (TDDFT) real-time domain simulation. We also compare these results to those of the systems with the same electron number but instead based on an ionic background (real lattice model). We demonstrate that a correspondence of plasmonic oscillation modes can be found between two similar systems with different models of background. However, the absorption energies of these plasmonic oscillations in jellium model are always larger than those in real lattice model by 0.1~0.4 eV. As the size of spherical structures increases, the absorption spectra and plasmonic oscillation modes, either in jellium or real lattice model, are also found to gradually reach to their classical limit of small size single sphere (dominated by dipole-oscillation).

This work shows that for Na metallic spheres with radius below ~1.5 nm, QM effects certainly have to be taken into account and the plasmonic behaviors cannot be well described by classical models.

A KKR Green’s function method is the one kind of the all electron first-principles electronic structure calculation method. In this method, instead of solving eigenvalue problem to construct electron charge density in each Kohn-Sham iteration, one-body Green’s function of crystal is directly calculated, and by taking imaginary part of its integration on complex energy plane, we can obtain electron charge density very accurately and efficiently. This is the main characteristics of this method.

The one-body Green’s function of crystal is calculated from arbitrary reference system by solving Dyson type equations. The reference system is defined as the system having the same lattice structure to crystal with different potential scatterer on each lattice positions. In the process of solving Dyson equation, this problem results in inverting a matrix of a dimension proportional to $N$ ($N$: the number of atoms in the unit cell). In the usual KKR method, a free space (no scatterer in whole the space) is chosen as the reference system. The analytical expression of the Green’s function for this free space reference system is known, and hence we can calculate desirable crystal Green’s function. However, when $N$ becomes large, the needed calculation increases drastically. This is because $O(N^3)$ calculations are required to invert a $N$ times $N$ matrix.

To overcome this difficulty, the concept of screened KKR was proposed. In the screened KKR method, a system with repulsive muffin-tin potentials of a constant height is chosen as the reference system. In this repulsive potential system, Green’s function decays exponentially in real space if the energy range is sufficiently lower than the repulsive potential height. Then we can ignore long range propagation without much loss of accuracy, the matrix which we must invert becomes sparse. Therefore, by combining with efficient sparse matrix solver, we can expect to improve calculation efficiency. This screened KKR method has been widely applied for multi layered systems assuming 2D periodicity within each layer until now.

To apply the concept of screened KKR for more general and complex systems, the real space screened KKR technique was proposed. In the real space screened KKR method, we concentrate on one atom in the system, and consider a surrounding local interaction region(LIZ) centered at this atom. All the multiple scattering effects are considered only inside this LIZ, and we have to calculate inverse matrix of the corresponding general block sparse matrix. The calculation for each LIZ centered on each atom in the system is independent, so these process is easily parallelized with respect to the number of atoms in the system. For this $O(N)$ property, it enables us to perform all electron first-principles electronic structure calculations of very large and complex systems.
Low temperature structure of filled ice hydrogen hydrate: an *ab initio* molecular dynamics study

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We present a study on the structural and vibrational properties of filled ice C2 hydrogen hydrate under compression by first principles molecular dynamics (FPMD). It is essential to be noted that the cubic Fd-3m space group [4] experimentally reported for C2 phase is the symmetry at high (room) temperature where the hydrogen bond network is disordered and the hydrogen molecules are orientationally disordered. In this sense, the “cubic” symmetry would definitely be lowered at low temperature where the hydrogen bond network is ordered and the hydrogen molecules are aligned. Indeed, we found tetragonal symmetry in our FPMD at low temperature. This finding demonstrates that the thermal effects play an essential role in the stabilization of the cubic structure. The vibrational frequencies are extracted from Fourier analysis of the MD trajectories, which are in good agreement with experimental data. Hydrogen bond is predicted to symmetrize below 60 GPa based on the analysis of O-H stretching frequencies and radial distribution function g(OH). In comparison with the pure ice VII, the hydrogen bond symmetrization pressure in C2 hydrogen hydrate is much lower as reduced by a factor two. We also observed an indication of transition to an unknown high pressure phase above 40 GPa.

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Low-temperature Phase Transitions in Ice by First-Principles Methods

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Experimental measurements on phase transition pressure of ice at low temperature limits have been reported several decades ago by Whalley\textsuperscript{1}, however, previous theoretical calculations using force fields have show it is far from trivial to reproduce these results\textsuperscript{2}. We perform density functional calculations to access the performance of commonly used DFT functionals on ice Ih, ice II, ice III, ice VI and ice VII. We compare different family of $E_{\text{xc}}$ without dispersions and obtain consistent results that do not agree well with experimental data. Effects from the contributions of phonon (zero-point energy) to free energy were examined and role of dispersion correction were accessed. Relevance of our calculated results with recent DFT calculations on the melting point between liquid water and ice will be discussed\textsuperscript{3}.

First-Principles Study on Doping and Electric Field Effects of Carbon Nanotubes on Hexagonal Boron Nitride Substrate

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It was recently shown that graphene becomes better when placed on a hexagonal boron nitride (hBN) substrate resulting in an increase in mobility and clear data in Quantum Hall measurements [1], and its electronic structure on hBN substrate was studied using scanning tunneling microscopy [2]. Using the density functional theory, we investigate the structural and electronic properties of pristine and doped (10,0) carbon nanotubes (CNTs) on the hBN sheet in the presence of an external electric field. Our study was initiated especially to answer whether the nearly-free electron (NFE) states originated from the hBN substrate would be brought down to the Fermi level, causing some problems in CNT devices. We consider different kinds and amounts of dopants to study the dependence on doping polarity and concentration. The electric field strength is adjusted from –0.2 V/Å and +0.2 V/Å to explore the effects of an external electric field on the electronic structures. Although the electronic energy bands of the hBN sheet are modified in accordance of the field strength, its NFE states do not approach down to the Fermi level under the field strength considered. We conclude that the hBN as a substrate does not modify the electronic structure of the CNT improving the device performance, compared with conventional substrate materials such as SiO₂.

Modeling of Punctured Nanotube Device Channels for Device Performance Enhancement

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Devices based on carbon nanotubes (CNTs) exhibit lots of experimental limits, since CNT network always consists of a mixture of metallic and semiconducting nanotubes. To improve the device characteristics, we perform device simulations based on sticks, which represent metallic or semiconducting CNTs. Especially we model unusual device channels containing several holes. We use the Monte Carlo simulations based on the percolation theory [1,2] to determine the device characteristics. We explore the dependences of the devices on CNT lengths, metallic-semiconducting ratios, channel dimensions, the sizes of punctured holes, and the number of holes on the device characteristics. We further evaluate quantitatively the device resistances. Our results show that the portion of semiconducting devices also increases, and the on/off ratio of the devices increases when the number of hole increases. Our model study agrees quite well with an experiment realized CNT network devices [3].

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Geometrical and Electronic Structures of Self-Assembled One-Dimensional Metal-Molecule Hybrid Chains: First Principle Study.

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We explore the geometrical and electronic structures of one-dimensional metal-molecule hybrid chain using \textit{ab initio} density functional theory. It is observed that such a hybrid chain is formed by spontaneous transformation from 4,4”-dibromo-p-terphenyl (DBTP) molecules when deposited on Ag (111) substrate at room temperature. We find that the chain is composed of p-terphenyl (TP) connected through an Ag atom to form (TP-Ag)$_n$. Our study shows that Ag (111) surface plays a catalytic role removing two Br atoms (DB) from DBTP and connecting the remaining TP through an Ag atom, which is a similar phenomenon as the Ullmann cross coupling reaction occurred on Cu surface. We considered various possible configurations of (TP-Ag)$_n$ on Ag (111) substrate to find most stable structure. We calculate the energy-dependent electronic structures exhibiting remarkably different charge distributions depending on the energy value related to the tip voltage in scanning tunneling microscopy (STM) experiments. Our results are very similar to the experimentally observed STM results. To simulate constant current mode of STM experiment we model the STM tip structure with a parabola, consider tunneling effect through the shape of tip. Our simulated STM images are very similar to the real STM images. Our further analysis on the geometrical and electronic structures is performed to understand the underlying physics in this system.

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Stable structures of adsorption Tl on the clean Tl/Si(111)

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Spin degeneracy is a consequence of both time-reversal and inversion symmetry. If the latter is broken, the degeneracy can be lifted (spin-orbit splitting) by spin-orbit interaction (SOI). Recently such spin splitting is commonly realized in the systems of two-dimensional electron gas (2DEG). The structural inversion asymmetry shows up at the surface or interfaces, and lead to spin split electronic state (Rashba-Bychkov effect). In particular, heavy metals on the light elements like Si show strong spin-orbit splitting and such property in Tl/Si(111) has been confirmed both in simulation and experiment [1]. This surface has been observed as a clean one. The stability of such surface has been investigated in the previous works.

In this study, the stable configuration of isolated Tl atoms on the surface of Tl/Si(111) has been investigated with using the first-principles approach in the generalized gradient approximation level. In this calculation, the pseudo-potential (PP) and plane-wave basis has been employed. The SOI is introduced by using fully relativistic PP [2].

There are several symmetry sites on the surface for atoms; hollow sites (T4, H3), bridge site, and top site (T1). We have optimized atomic structure of surfaces and compared the total energies. The T4-site model has been found to be the most stable in the systems investigated. In the presentation, we will report details of the stable structure and, for typical systems we will also represent electronic structures and spin splitting in the band dispersion relations. The SOI effects on the atomic structure will be discussed by comparing between the results with and without SOI.

We report on schemes that improve the convergence of the selfconsistency cycle in density functional theory (DFT) calculations. We implemented these schemes employing the projector augmented wave (PAW) method [1,2] and the real-space finite difference method [3] that aims for the computation of large systems. On this poster, we focus on the relaxation of rotated magnetic directions in noncollinear systems, and on inter-atomic forces.

The search for the ground state of complex noncollinear magnetic systems can be very cumbersome, as the energy differences between configurations with differently rotated magnetic moments are very small. Therefore, the directions of the atoms' magnetic moments might relax rather slowly during the DFT selfconsistency cycle (that is based on energy minimization). We improved the convergence in such cases by extending the metric of the well-known Broyden density mixing scheme [4].

Although it is straightforward to obtain the total energy and inter-atomic forces from a well-converged charge density, in practice it is also desirable to minimize the error in the energy and force calculations that are based on not fully-converged densities and Kohn-Sham states. In this case one has to distinguish between the input density (used to construct the Hamiltonian) and the resulting output density (constructed from the eigenstates of that Hamiltonian). If the total energy and forces calculations are based only on the output density and the corresponding wavefunctions, the errors are relatively small and relatively few selfconsistency cycles are required. This is easily taken into account in the energy calculations of most DFT schemes, but requires some caution in PAW force calculations.

First-principles calculation of transport properties of Al/GaN interface

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Gallium nitride (GaN) is a wide bandgap semiconductor attracting significant attention due to its possible applications to semiconductor devices such as diodes, LEDs and solar cells. Since semiconductor devices are always contacted with metallic electrodes, transport properties of metal-semiconductor interfaces are vitally important for device development. One troublesome phenomenon is the Schottky barrier generated in the interface that prevents current flow and reduces device performance. Hence a large number of experimental efforts have been made to minimize this effect when a new device is developed. For more efficient developments of devices, introducing quantum simulations based on first-principles calculations is one of the most promising techniques.

A heterojunction like metal-semiconductor interface can be considered as a multilayered system since there exists a two-dimensional translation symmetry within a plane parallel to the interface. It however is still difficult to calculate the electronic states of multilayered structures by first-principles calculation. It is because that the unit cell to be dealt with is elongated along one-direction and thus contains many atoms, which makes the computational cost rather high.

The screened KKR method [1] can solve the Kohn-Sham equations efficiently especially for multilayered systems. Furthermore, by implementing the Kubo-Greenwood formula [2] into the screened KKR, we have realized fast first-principles calculation of the conductivities of multilayered systems.

In this presentation, we will show the results of our recent calculations on the transport properties of Al/GaN contacts. This is a new application of our method to materials design of GaN devices.

Enhancement of magnetism of Fe by Cr and V

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The Curie temperature of bcc FeV and FeCr alloys with a small content of V or Cr is higher than that of pure bcc Fe, whereas their saturation magnetizations are smaller than that of Fe \cite{1}. Although this has been experimentally known for a long time, not much attention has been paid to it so far and the origin of this increase has not been yet clarified.

In the present study, we discuss the origin of the enhancement of magnetism of Fe by adding Cr/V on the basis of the first-principles electronic structure calculation. The Cr/V $d$ states are located at higher energy region than those of Fe. This causes the $d$ states of Fe next to Cr/V to be pushed down to the lower energy side compared to those of pure Fe due to the hybridization with Cr/V. Thus “mutated” Fe atom enhances the magnetic moment of other Fe atoms as well as the exchange coupling among them. This mechanism is similar to the enhancement of the magnetism in FeCo alloys \cite{2} and Fe alloyed with typical elements \cite{3}. Based on this idea, we extend the theory towards designing new type of permanent magnets that can be used at higher temperatures and are free from rare earth elements.

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Analyses of relationships between stacking structures
of $sp^3$ network materials and their band gaps

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Silicon carbide (SiC) has been discovered in various polymorphs. The polymorphs are characterized by the stacking of atomic planes. The band gaps vary substantially in each polymorph from 2.40 eV to 3.33 eV in spite that the local atomic structures are identical to each other [1]. The mechanism of this intriguing property have been poorly understood. In this study, our purpose is to clarify the band-gap variation sensitive to the tiny structural difference and examined whether this feature is common to other $sp^3$-bonded materials. Calculations were performed in the GGA in the DFT.

Figure I shows the calculated energy bands of SiC polymorphs. Apparently, the conduction bands of the three polymorphs are qualitatively different. We found the large band-gap variation was related closely to the character of the Kohn-Sham orbital at the conduction-band minimum, and the variation was seen in other $sp^3$-bonded materials as well [2]. The details are presented in this poster.

![Figure 1: Calculated band structures of Silicon carbide (SiC)]

References

Comparative study of hybrid functionals applied to condensed matters: structural and electronic properties

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Density functional theory with its local density approximation (LDA) and generalized gradient approximation (GGA) has achieved great success in understanding and predicting properties of materials. However, these approximations underestimate energy band gaps of semiconductors and insulators, and fail to describe some of the properties including ground-state magnetic ordering for some transition-metal oxides. Improvements of the approximations are highly demanded in the fields of condensed matter physics and materials science. The hybrid functionals, combining LDA or GGA with the Hartree-Fock approximation (HFA) would be effective to break limitations of LDA and GGA. Recently, a success of application of Heyde-Scuseria-Ernzerhof (HSE) functional [1] to extended systems has been reported [2], but the materials and also the functionals examined are still quite limited.

In the present study, we present a comprehensive study about performance of several hybrid functionals, including the Perdew-Burke-Ernzerhof-free (PBE0) [3], HSE, and long-range corrected (LC) hybrid functional [4]. We have implemented the hybrid functional scheme in our well-established plane-wave-basis-set ab initio band-structural code, TAPP, and examined 10 prototype semiconductors and insulators. For structural parameters, hybrid functionals generally give better agreements with experiments than GGA; in HSE functional, the lattice constants and the elastic constants are well described within 1.39 % and 5.4 % accuracy, respectively, with respect to experimental values. LC functional reproduces the lattice constants within 1.21 % and the elastic constants within 5.5 %. Figure 1 compares theoretical band gaps based on GGA, HSE, and LC with the experiments. It is clear that the use of the hybrid functionals improve the underestimate in GGA substantially [5, 6].

References
First-principles study of the electric double-layer capacitance at water-graphene interfaces

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Electric double-layer (EDL) is known as an important stage for electrochemical reactions at electrode-liquid interfaces. It has also attracted growing interest for its applications to electronic devices, called EDL capacitors (supercapacitors) and EDL transistors. The former is a promising device of power electronics and green-energy storages [1]. The later device is a versatile tool to induce electronic phase transitions by changing the electronic charge accumulation. Indeed, the observation of field-induced superconductivity on ZrNCl with the use of the device was reported [2].

In application of each device, predicting the capacitance at liquid-solid interface is required. In the early 1900s, Gouy and Chapman proposed a fundamental EDL model, which is equivalent of the Debye-Hückel theory [3]. The modification of their theory, due to Stern, is taking experimental account of the finite size of ions nearby the surface [4]. However, these models contain no information of the microscopic structure of the EDL. Helmholtz capacitance, the part of the EDL capacitance depending on the microscopic structure, has still not been predicted theoretically.

To predict the Helmholtz capacitance by treating the microscopic structure of solid-liquid interface theoretically, we calculated the structure of water-graphene interfaces by using first-principles molecular dynamics with effective screening medium (ESM) method [4,5]. We can simulate both the electronic structure and the atomic configurations under the condition of the charged electrode through the use of the ESM method. As a result, we made it possible to estimate the Helmholtz capacitance taking the effect of the molecular orientation of the water and the electronic polarization in the water molecules due to the electric field into consideration theoretically. Apparent dielectric constant of the water near the interface can be also calculated. The results show that contribution of the dipole caused by the molecular orientation of the water is larger than that of the electronic polarization due to the electronic field, which is reasonable compared with a classical theory.

Magnetism and Transport Property of Graphene on Substrates

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Recently, it was experimentally reported that the carbon atom of the graphene has induced magnetic moment on Ni(111)\textsuperscript{[1]}. Understanding the magnetic interaction between the graphene and magnetic electrodes or substrates is important for spintronics-device applications of graphene. It is expected that the magnetic coupling between graphene and magnetic electrode or substrate significantly affect the electronic structure and transport properties of graphene.

In this study, we have performed first-principles non-collinear density functional calculations of graphene and graphene nanoribbon on substrates. We clarify how magnetic electrodes or substrate affect the electronic structure and magnetism of graphene. We find that the magnetic moment of the edge C atom in the mono-layer ZGNR on Ni(111) layer is very small. In the case of the ZGNR over a graphene sheet on Ni(111), the magnetic moment of the edge C atom at the ZGNR maintains and the ferromagnetic state is stable. We will discuss the effect of spin-orbit interaction and noncollinear magnetism on transport properties of graphene and graphene nanoribbon.

Band-Gap Engineering of Hydrogen-Potassium Graphite Ternary Intercalation Compound Thin films

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Graphite is known to be a starting material for various compounds in which the nanometer-scale or low-dimensional carbon network play decisive role for determining their physical and chemical properties. Among them, graphite intercalation compounds (GICs) are the one of representative and legendary materials possessing interesting physical properties. The geometric structure of the GIC is characterized by the layered structure in which the graphene and intercalant are alternatively stacked normal to the plane. In this work, we demonstrate the possibility of band gap engineering of graphite thin films in terms of the intercalation of a hydrogen-potassium complex based on DFT-LDA calculation. The complex is known to be a ternary GIC compound, KH-GIC, and has been synthesized in the previous experiment [1]. Here we consider the KH-GIC thin film with stage-2 structure comprising a pair of bilayer graphene and the KHK layer as shown in Figure. In the structure, due to the intrinsic dipole moment of sandwiched KHK layer, bilayer graphene possesses finite energy gap between π-band and π*-band at the K point. The result indicates the possibility of band gap engineering in thin films of graphite by considering the legendary compound of graphite. Although the system is a metal due to the charge transfer from K to C, hole injection into the compound results in the semiconducting graphite with finite energy gap which could be applicable as the constituent for the semiconductor switching devices.

\textbf{bilayer graphene}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{schematic.png}
\caption{Schematic picture of slab model of hydrogen-potassium graphite ternary intercalation compounds. In the model, potassium atoms and hydrogen atoms are put between bilayer graphenes.}
\end{figure}

From first-principles approaches, we show that the current-induced forces and the approximate selection rule for inelastic effects are highly relevant to the current density in an asymmetric molecular junction. The curved flow of current streamline around the asymmetric molecule may induce a net torque, which tends to rotate the molecule, similar to the way a stream of water rotates a waterwheel. Thus, such molecular junction offers a practical system in the exploration of the possibility of atomic-scale motors. We also illustrate examples to demonstrate the misjudgment of the importance of normal modes by employing the approximate selection rule based on the current direction.
Controlling chemical reactivity of ultrathin oxide film by interface manipulation

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Ultrathin oxide films grown on metal substrate are of great interest not only as supporting materials for chemically active nanoparticles but also as catalysts in the field of heterogeneous catalysis [1]. Using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we have demonstrated that the chemical reactivity for water dissociation on an ultrathin MgO film grown on Ag(100) substrate depends greatly on film thickness and is enhanced as compared to that achieved with their bulk counterpart [2]. The change of chemical reactivity of ultrathin MgO film depending on the film thickness can be explained by the strengthening of the interaction between the oxide and metal interface layers. This result implies that the artificial manipulation of the local structure at the oxide-metal interface is expected to play a pivotal role in controlling the catalytic activity of oxide film. Therefore, water dissociation on three model systems with defects at the oxide-metal interface of the 2-ML MgO/Ag(100) - an O vacancy (Fig. 1a), an Mg impurity, or an O impurity - has been examined and compared with the case of a MgO film without defects using periodic DFT calculations [3]. Our results clearly show that such structural imperfections at the interface can improve the chemical reactivity of ultrathin MgO film supported by Ag(100) substrate. This is closely correlated with the accompanying change of charge distribution of the oxide surface due to the accumulation of transferred charge density at the interface (Fig. 1b). In addition, the chemical reactions on the ultrathin oxide film surface can be tuned by interface defects regardless of the charging of adsorbates. Our study about water dissociation on MgO/Ag(100) not only reveals the potential of an ultrathin oxide film as a catalyst but also opens new vistas for the development of techniques to control and measure the interface structure of oxide film deposited on a metal substrate.

Fully relativistic calculation of Bi (001) films without inversion symmetry

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The Spin-Orbit interaction (SOI) is very important for heavy atom like Bismuth. Recently, first-principles study revealed that significant SOI effects on the electronic structure and lattice bistability of Bi nanofilms.¹

In this study, we perform first-principles electronic structure calculations under the electric field for Bismuth thin film and Bi (001) multi-layer surface. We revealed that the SOI combined with electric field (so called Rashba effect) is very important in Bi surface state and Bi edge state. We calculate spin polarization and spin direction for each band and k-points.

Fig. 1(a) shows the band structure near the Fermi level of 1 bilayer-Bi (001) film when the electric field applied. The magnitude of applied electric field is |E|=20(GV/m) and the direction is perpendicular to Bi (001) surface, and upward. Fig. 1(b) shows the in-plane spin direction distribution at each k-point below the Fermi energy -0.5(eV), and fig. 1(c) is the enlargement figure of fig. 1(b). The red arrows show up spin, and blue arrows show down spin.

Recently, giant out-of-plane spin component on Bi (001) surface is discovered SR-ARPES experiment.² We also calculate the spin structure of multi-layer Bi (001) surface, and our calculated result shows the detail of spin features at each k-point.

Origin of Multiple Conductance Peaks in Single-Molecule Junction Experiments

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One of the most important yet unresolved problems in molecular electronics is the controversy over the number and nature of multiple conductance peaks in single-molecule junctions. Currently, there are three competing explanations of this observation: (1) manifestation of different molecule-electrode contact geometries, (2) formation of gauche defects within the molecular core, (3) involvement of different electrode surface orientations [1]. However, the exact origin of multiple conductance peaks is not yet fully understood, which indicates our incomplete understanding of the scientifically as well as technologically important organic-metal contacts. To theoretically resolve this problem, we previously applied a multiscale computational approach that combines force fields molecular dynamics (FF MD), density functional theory (DFT), and matrix Green’s function (MGF) calculations [2] to a thermally fluctuating hexanedithiol (C6DT) molecule stretched between flat Au(111) electrodes, but could observe only a single conductance peak [3]. In this presentation, using DFT geometry optimizations and MGF calculations, we consider molecular junctions with more realistic molecule-metal contact conformations and two different Au(111) and Au(100) electrode surface directions. We find that both different S-Au coordination numbers and electrode surface orientations can in principle contribute to the formation of multiple conductance peaks, but conclude that the S-Au coordination number should be the more dominant factor than the electrode surface orientation.

References:
Material design for superconductivity on semiconducting boron

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Aside from prediction of $T_c$, the most important role of material design for superconductivity research is very similar to that of other field. Given a candidate for high-$T_c$ material, how synthesize the candidate is a big problem for experimentalists, for which material design has to answer. Many people believe that diamond could have high $T_c$ around 40 K, if a sufficient level of doping is achieved. This is the most serious problem. Crystal growth and related techniques are somewhat dirty subjects, and thereby these are the last one which theorists try to study. The strategy of the present author for this is use of combination of first-principles calculations and thermodynamic consideration. This is an extremely powerful tool for material researches.

In this paper, the author's experience on superconductivity research is presented form the standpoint of material design. A special topic is chosen in the superconductivity of semiconductors, especially, those of high refractory materials such as C and B, because of the strong electron-lattice interactions.

Boron is particularly interesting because of its exotic structure, that is, icosahedron-based structure. It is expected to exhibit a high $T_c$ superconductor, if the matrix is made to be metallic. The most common phase of boron, $\beta$ boron, was proven to undergo superconductivity transition at high pressure (160 GPa). However, crystal structure at such high pressures has yet been clarified. Even phase diagram of boron was not known. Therefore, establishment of the phase diagram of boron is of emergent importance.

The first thing to do was determination of the phase diagram. We are the first to predict the phase diagram of boron. Since then, a profound progress has been achieved in this field. Discovery of a new phase of $\gamma$-boron, new idea of frustrated systems are such examples.

Based on our prediction of the phase diagram, we know that $\alpha$ phase is the most stable phase at high pressure. It is advantageous to examine superconductivity of $\alpha$ phase at high pressures, because of its stability. In addition, the structure of $\alpha$ phase is relatively simple. With these benefits, the author led experimentalists to study superconductivity of $\alpha$ phase. Our collaborators finally discovered the superconductivity of $\alpha$ phase at high pressure. Significant progress has been achieved regarding the metallization mechanism. Of further importance, we have theoretically solved a difficult issue of doping to $\alpha$ phase. An efficient method of doping is use of high pressure. Experimentalists are almost about catching of this doping.

Review references