

Abstracts

Oral presentations

Recent progress in first-principles simulations of water

Roberto Car

*Department of Chemistry and Department of Physics, Princeton University, Princeton, New Jersey
08544, USA*

Modeling water from first principles has been very challenging for a long time, as physical effects beyond the reach of standard density functional theory based molecular dynamics cannot be neglected. Only recently could simulations assess the structural role played by hybrid functionals, dispersion interactions, and quantum dynamics of the nuclei. These studies will be reviewed and compared to old and new experimental data.

In addition to diffraction (x-ray, neutron), core excitation spectroscopy has emerged as a powerful tool for investigating hydrogen bonded systems. Accurate simulations of the x-ray absorption spectra in disordered molecular materials are very demanding in view of the accurate treatment of the electronic excitations that they require. This difficulty has greatly hampered the interpretation of experiments. Novel calculations of the x-ray absorption spectra of water, crystalline ice, low- and high-density amorphous ices, including the effects of nuclear quantum dynamics and of local field screening will be presented. These studies achieve unprecedented agreement with experiment, showing the underlying electronic and structural features that are behind the observed spectra in all these systems.

Finally, prospects and future challenges for *ab-initio* simulations of condensed molecular systems will be discussed.

Universal Features in Band Structures of Crystalline and Amorphous Transparent Conducting Oxides

Youngho Kang¹, Sang Ho Jeon¹, Young-Woo Son² and Seungwu Han¹

¹*Department of Materials Science and Engineering, Seoul National University,
Seoul 151-744, Korea*

²*Korea Institute for Advanced Study, Seoul 130-722, Korea*

Transparent conducting oxides (TCOs) such as ZnO, In₂O₃, SnO₂, and their compound structures are well known for unique combination of opposing material properties of the high conductivity and optical transparency, which enables their wide use in various display and energy devices. Recently, the amorphous phase of compound TCOs such as InGaZnO has been actively studied for applications to channel layer in TFT used in next-generation display. In spite of the atomic disorder inherent in the amorphous phase, the electron mobility is comparable to those in typical crystalline materials. Several first-principles calculations have been performed on TCOs and it has been found that conduction bands of these materials look very similar in spite of disparate atomic structures. Furthermore, the pseudo-band structures of the amorphous phase also show a crystalline band structures, implying that the k -vector could be a good quantum number in the amorphous phase in spite of the atomic disorder. Even though it has been speculated that s orbitals of metal atoms contribute to the insensitivity to the atomic disorder, full microscopic analysis has not been carried out yet.

In this presentation, using a tight-binding model, we will analyze the electronic structures of conduction bands in various TCOs. We find that the O p orbital plays an important role in the band structure, particularly for high concentration of electron carriers. We explicitly prove that as long as the crystalline local order is preserved in the amorphous phase, the extended Bloch-like states correspond to the eigenstates of the Hamiltonian. The constructed Hamiltonian shows a universal form and the energy dispersion relation resembles that of massive Dirac particles. Therefore, at high electron concentrations, the energy band is well approximated as a three-dimensional linear band. The electron mobility of crystalline ZnO is also calculated based on the new band structure and in consideration of various scattering mechanisms.

Cation Composition Effects on the Electronic Structures of Amorphous Oxide Semiconductors

Yong-Sung Kim¹, Ho-Hyun Nam¹, and Dae Hwan Kim²

¹*Korea Research Institute of Standards and Science, Daejeon 305-340, Korea*

²*School of Electrical Engineering, Kookmin University, Seoul 136-702, Korea*

The electronic structures of amorphous oxide semiconductors are investigated based on density-functional theory (DFT) calculations. The In, Sn, Ga, and Zn cations are considered with various composition ratios [1,2]. The conduction band minimum (CBM) states are mainly affected by the In and Sn cations. As the In and Sn cation ratios increase, the CBM is found to be lowered, and correspondingly the electron effective mass is reduced. The valence band tail (VBT) states are also affected by the cation compositions. Interestingly, the VBT states are increased, as the In and Sn ratios increase. The VBT evolutions are found to be due to the O-2p inter-site coupling, which depends on the cation compositions. The VBT states are also contributed by the Zn-3d and O-2p hybridization as a secondary effect. We discuss the conductivity and reliability issues of AOS based on the DFT results.

[1] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, *Nature* 432, 488 (2004).

[2] C. W. Ow-Yang, H. Yeom, and D. C. Paine, *Thin Solid Films* 516, 3105 (2008).

Spin-polarization and magnetism in cubic silicon carbide

Mingwen Zhao, Yueyuan Xia, and Liangmo Mei

*School of Physics and State Key Laboratory of Crystal Materials, Shandong University, Jinan
250100, China*

In contrast to the conventional magnetic materials which contain d or f electrons, pure carbon materials, such as graphite, which have only s and p electrons can also achieve electron spin-polarization and even room temperature ferromagnetism [1]. Both theoretical and experimental works have confirmed that this carbon magnetism is closely related to the vacancy defects which break locally the continuity of conjugate π orbitals [2]. Using ion-implantation technique, one can control the structure, density, and distribution of the vacancy defects, to achieve strong magnetism in graphite.

In this presentation, we will report our first-principles calculations of the electron spin-polarization in silicon carbide (SiC) crystals. Our results show that the silicon vacancy defects (V_{Si}) in cubic SiC crystal have stable high spin states. The magnetic moment of V_{Si} defect depends on the charge states. The coupling is ferromagnetic between the V_{Si} defects at $-2e$ charge state, whereas the V_{Si} defects at $-e$ charge state prefer to interact antiferromagnetically [3]. Substituting C with N atoms can manipulate the charge states of V_{Si} defects and the magnetic interactions between them. Hund's rule combined with a super-exchange model is available for understanding these results. Moreover, we predict that when a N atom occupies a C site (N_C defect) in 3C-SiC, it tends to form a $N_C V_{Si}$ centre with an adjacent V_{Si} . Electronic structure calculations indicate that this $N_C V_{Si}$ centre can be regarded as an analog of the famous NV centre in diamond, and thus has potential applications in solid quantum-bite (qubit) operations [4]. On the other hand, when Si atom in 3C-SiC crystal is substituted by Al atom (Al_{Si} defect), an $Al_{Si} V_C$ centre composing of two adjacent Al_{Si} and carbon vacancy (V_C) defects is preferred. Although, the local symmetry of the $Al_{Si} V_C$ centre (C_{3v}) is the same as that of the $N_C V_{Si}$ centre, their electronic structures are quite different. The defect levels of $Al_{Si} V_C$ centre reside in the valence bands and conduction bands and thus are unsuitable for qubit operations [5]. A simple model associated with group theory analysis is presented to address the physical origin of these results.

- [1] H. H. Xia, W. F. Li, Y. Song, X. M. Yang, X. D. Liu, M. W. Zhao, Y. Y. Xia, C. Song, T. W. Wang, D. Z. Zhu, J. L. Gong, Z. Y. Zhu, *Adv. Mater.* 20, 4679(2008).
- [2] X. M. Yang, H. H. Xia, X. B. Qin, W. F. Li, Y. Y. Dai; X D. Liu, M. W. Zhao, Y. Y. Xia, S. S. Yan, B. Y. Wang, *Carbon* 47, 1399 (2009).
- [3] M. W. Zhao, F. C. Pan, L. M. Mei, *Appl. Phys. Lett.* 96, 012508 (2010).
- [4] F. C. Pan, M. W. Zhao, L. M. Mei, *J. Appl. Phys.* 108, 043917 (2010).
- [5] X. P. Wang, M. W. Zhao, H. H. Xia, S. S. Yan, X. D. Liu, *J. Appl. Phys.* 110, 033711 (2011).

[S-02]

Structure prediction of clusters and solids by the minima hopping global geometry optimization method

Stefan Goedecker

Department of Physics, Universität Basel, Klingelbergstr. 82, 4056 Basel, Switzerland

The minima hopping global geometry optimization method will be introduced together with the fundamental principles on which it is based. Various applications of the method will be presented and in particular applications where the potential energy landscape is explored on the density functional level. In particular, it will be shown that many theoretically proposed structures for endohedral silicon cages and boron fullerenes are only metastable structures and that the energy landscape for these systems is quite different from the landscape of structures which can be synthesized in experiment. Finally some new results on the structural richness of some simple crystalline materials will be presented.

Ab-initio random structure search for metallic clusters

C. M. Chang¹, J. P. Chou², C. R. Hsing², C. M. Wei², and C. Cheng³

¹*Department of Physics, National Dong Hwa University, Hualien 974, Taiwan*

²*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan*

³*Department of Physics, National Cheng Kung University, Tainan 701, Taiwan*

The 13-atom metal clusters of fcc elements (Al, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au) are studied by density functional theory calculations. The global minimum configurations were searched by the ab-initio random structure searching method [1], and we have found new lowest-energy structures for Ni₁₃, Pd₁₃, and Au₁₃ clusters. We have also found that elements with higher ratio of dimer-to-bulk nearest neighbor (NN) bond length would have higher effective coordination numbers (ECN) for the lowest energy structures of the 13-atom clusters (except for Au₁₃ which is believed to have a high relativistic effect). From the relationship between the ECN and the ratio of dimer-to-bulk NN bond length, we can identify two distinct groups for the lowest energy structures: 1.) Compact like structures with triangular motifs are preferred for elements that without d-electrons or with (nearly) filled d-electrons (Ni, Pd, Cu, Ag, Al); 2.) Non-compact structures with both square and triangular motifs are preferred for unfilled d-band elements (Rh, Ir, Pt).

[1] C. J. Pickard and R. J. Needs, *J. Phys: Condens. Matter*, **23**, 053210 (2011).

First-Principles Modeling of Deformation and Diffusion

Shigenobu Ogata¹

¹*Department of Mechanical Science and Bioengineering, Osaka University, Toyonaka, Osaka 560-8531, Japan*

Recent progress of nanoscale materials processing, testing and observation techniques enables to discover mechanical behaviors of materials having nanoscale characteristic length [1]. First-principles nanoscale atomistic modelings and simulations are promising ways to understand the fundamental mechanisms of the mechanical behaviors. Here the following three first principles atomistic modelings regarding deformation and diffusion in materials at nanoscale are introduced: 1) hydrogen and carbon diffusion analyses in metal by path-integral and accelerated molecular dynamics methods[2-4], 2) nonlinear elastic constitutive equation for crystals by first principles density functional theory method, and 3) creep deformation of nanocrystalline metal by molecular dynamics method[5-6].

[1] T. Zhu, J. Li, S. Ogata, S. Yip, MRS Bulletin 34, 167 (2009).

[2] H. Kimizuka, H. Mori, and S. Ogata, Phys. Rev. B 83, 094110 (2011).

[3] H. Kimizuka and S. Ogata, Phys. Rev. B 84, 024116 (2011).

[4] A. Ishii, S. Ogata, and J. Li, submitted.

[5] Y. Wang, A. Ishii, and S. Ogata, Mater. Trans, to be published.

[6] Y. Wang, A. Ishii, and S. Ogata, submitted.

[A-06]

Electronic Structure of Twisted Multilayers of Epitaxial Graphene

Mei-Yin Chou^{1,2}, Lede Xian¹, Zhengfei Wang¹, Jia-An Yan³, Wen-Ying Ruan¹, and Salvador Barraza-Lopez¹

¹*School of Physics, Georgia Institute of Technology, Atlanta, Georgia, USA*

²*Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan*

³*Department of Physics, Astronomy and Geoscience, Towson University, Towson, Maryland, USA*

Epitaxial growth of graphene on the carbon face of the SiC substrate has produced an interesting system of quasi-ordered multilayers. It is intriguing that the results of quantum Hall and angle-resolved photoemission measurements for this multilayer system all exhibit physical properties that resemble single-layer graphene. This is believed to arise from the particular rotational stacking pattern in which the Bernal AB sequence is interrupted (twisted) by interleaved layers that are rotated by an angle θ . In this talk, I will discuss our computational efforts that investigate the special electronic properties of few-layer graphene, such as the fractal features in the Landau levels of twisted bilayer and the surface states in ABC-stacked few-layer graphene. In addition, we have studied the interaction between twisted graphene layers in various triple-layer systems using density-functional-theory calculations. We demonstrate that the coupling in certain twisted triple-layer systems has quite different behavior compared to twisted bilayer systems, which reveals that the coupling between layers albeit weak is still important in determining the electronic properties of the whole system. These results shed light on the anticipated electronic structure of this particular rotated multilayer graphene system.

Topological phase in Dirac fermionic heterostructures

Seung-Hoon Jhi^{1,2}, Jinwoong Kim¹, Jeongwoo Kim¹, Kyung-Hwan Jin¹, and Kiseok Kim^{1,3}

¹*Department of Physics, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea*

²*Division of Advanced Materials Science, POSTECH, Pohang 790-784, Republic of Korea*

³*Asia Pacific Centre for Theoretical Physics, POSTECH, Pohang 790-784, Republic of Korea*

Topological phase 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 intriguing 2D electronic structures and attract great attention for potential application to electronic devices.

Here we discuss the topological phase transition and the proximity effect in the heterostructures of Dirac fermions. Understanding phase transitions between topological and non-topological states of matter has been pursuit since the discovery of topological insulator. Using first-principles methods and model Hamiltonian, we studied topological phase transition in superlattice of topological insulator and band insulator (BI). Superlattice of TI and BI comprised of chalcogenide creates 1D array of interacting Dirac fermions. We show that this interacting 1D Dirac-fermionic superlattice undergoes the band insulator – topological insulator transition depending on the TI-BI coupling strength, the mass gap, and the band gap of BI layer. These parameters are, in turn, controlled by external strain and/or layer thickness.

Heterostructures of graphene and TI also provide interesting platforms to explore exotic electronic and transport properties of Dirac materials. In the second part, we present the electronic structure of graphene in contact with TI. The Dirac cones of graphene on the TI surface show several interesting features including band gap-opening and splitting. Using the first-principles calculations and tight-binding method, we analyzed the origin of the changes in the Dirac cones and found that both intrinsic and extrinsic spin-orbit couplings are enhanced significantly due to proximity to topological insulator.

Half-metallic Surface States and Topological Superconductivity in NaCoO₂

Hongming Weng¹, Gang Xu¹, Hangjun Zhang², Shou-Cheng Zhang^{2,3}, Xi Dai¹, and
Zhong Fang¹

¹*Beijing National Laboratory for Condensed Matter
Physics, and Institute of Physics, Chinese Academy of Sciences,
Beijing 100190, China*

²*Department of Physics, McCullough Building, Stanford
University, Stanford, CA 94305-4045*

³*Center for Advanced Study, Tsinghua
University, Beijing, 100084, China*

Majorana fermions obey non-Abelian statistics, which is the key ingredient for the fault-tolerant topological quantum computation. Recently, they have been proposed to exist in various condensed-matter systems as emergent excitations[1]. However, experimental realization in these materials remains challenging. For a half-metal, which acts as conductor for one spin and insulator for another spin, the proximity effect with a *s*-wave superconductor can induce topological p_x+ip_y superconductivity and Majorana fermions in the vortex core[2]. In this work we predict a novel half-metallic surface state in layered bulk insulator NaCoO₂, with tunable surface hole concentration. The half-metallic surface has a single fermi surface with a helical spin texture, similar to the surface state of topological insulators, but with the key difference of time reversal symmetry breaking in the present case. We propose realization of topological superconductivity and Majorana fermions when the half-metallic surface states are in proximity contact with a conventional superconductor [3].

[1] M. Franz, *Physics* **3**, 24 (2010).

[2] S. B. Chung, H. Zhang, X. Qi, and S.-C. Zhang, arXiv:cond-mat/1011.6422 (2010)

[2] H. Weng, G. Xu, H. Zhang, S.-C. Zhang, X. Dai, and Z. Fang, *Phys. Rev. B* **84**, 060408(R) (2011)

Reactivity of valence band holes at the rutile TiO₂/water interfaceJun Cheng, Michiel Sprik*Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom*

Photo-active wide gap metal oxides, such as TiO₂, have remarkably deep lying valence band maxima (VBM). The VBM of aqueous rutile TiO₂ is -7.1 eV at PZC (the pH for which the net proton charge of a surface vanishes. PZC=5 for rutile TiO₂ (110)). An ionization potential of 7.1 eV corresponds to an electrode potential of 2.6 V vs the normal hydrogen electrode (NHE). Free holes should therefore be just about able to oxidize a water molecule to a hydroxyl radical, which requires a minimum potential of 2.4V vs NHE at PZC. Such photo-generated hydroxyl radicals are considered to act as intermediates in the photo-oxidation of aqueous pollutants by titania. However, self trapping of free holes is assumed to be a fast process, reducing the oxidative power of a photogenerated hole. As a result, photo-excitation may not produce enough energy for dehydrogenation of water molecules in the bulk liquid. This raises the question whether dehydrogenation of a water molecule adsorbed on the TiO₂ surface is easier.

We have investigated this question using the latest advances in the CP2K code (cp2k.berlios.de), which allows us to use hybrid density functionals containing a fraction of exact exchange. Indeed, under PZC and flatband conditions, we find that adsorption at the aqueous (110) interface reduces the dehydrogenation potential of a water molecule by 0.5V. However, the hole trapping energy was found to be almost the same. Therefore, according to our calculations, the oxidative power of the self-trapped hole matches the dehydrogenation energy of an adsorbed water molecule. The implication is that photogenerated holes have little surplus energy to overcome possible overpotentials for abstraction of an hydrogen atom from water. After an outline of the density functional theory based molecular dynamics method (DFTMD) we have applied[1,2], we will analyze these perhaps somewhat unexpected results by an energy decomposition method borrowed from the study of homogeneous proton coupled electron transfer (PCET) reactions[3].

[1] J. Cheng, M. Sprik, *J. Chem. Theory Comp.* 6, 880 (2010).

[2] J. Cheng, M. Sprik, *Phys. Rev. B* 82, 081406R (2010).

[3] F. Costanzo, M. Sulpizi, R. G. Della Valle, M. Sprik, *J. Chem. Phys.* 134, 244508 (2011).

[A-09]

Time-dependent density functional method for studying electron transfer at solid-molecule interfaces

Woo Youn Kim¹, Danilo Nitsche², and G.K.U. Gross²

¹*Department of Chemistry, KAIST, Daehak-ro 291, Yuseong-gu, Daejeon 305-701, Korea*

²*Theoretical Department, Max-Planck-Institute of Microstructure Physics, Weinberg 2, Halle D-06120, Germany*

Electron transfer plays a key role in various types of chemical reactions. In particular, interfacial electron transfer between molecules and a solid electrode is attracting great interests for diverse applications such as molecular electronics, dye-sensitized solar cells, fuel cells, etc. Experimental investigation on the process of such electron transfer, however, is not simple, since it occurs on a solid surface under non-equilibrium condition within a few tens to hundreds femtoseconds. In this regard, theoretical methods offering a tool to study ultrafast electron dynamics in a time-dependent manner would be useful as a complement. We note that those methods, however, have certain limitations when they are applied to the interfacial electron transfer, since they rely on a finite size model (such as a slab or atomic clusters) to describe semi-infinite electrodes. Herein, we propose a new approach based on real time time-dependent density functional theory that is able to effectively treat semi-infinite nature of an electrode by incorporating the exact time-propagation of electron wavefunctions at the boundary between molecules and an electrode.

Time-Dependent Density Functional Theory for Femtosecond Electron Dynamics in Dielectrics

K. Yabana^{1,2}, Y. Shinohara², T. Sugiyama², T. Otobe³, G.F. Bertsch⁴

¹*Center for Computational Sciences, University of Tsukuba, Tsukuba 305-8571, Japan*

²*Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan*

³*Advanced Photon Research Center, Japan Atomic Energy Agency, Kyoto 619-0215, Japan*

⁴*Department of Physics, University of Washington, Seattle, U.S.A.*

In recent optical science, time-domain explorations of ultrafast quantum dynamics in femto- to atto-second time-scale have been one of the central subjects. We have been developing a first-principles computational approach for electron dynamics in molecules and solids by solving time-dependent Kohn-Sham equation in real-time. In my presentation, I would like to present our recent progresses in describing electron dynamics in dielectrics induced by intense and ultrashort laser pulses.

To describe interaction between conduction electrons and laser electric field, we must consider coupled dynamics of electrons and electromagnetic fields when the laser electric field is so strong that one cannot apply a perturbation theory. In dipole approximation, one needs to solve coupled equations for macroscopic polarization and electrons [1]. We have applied the formalism for coherent phonon generation [2] and optical dielectric breakdown [3].

As for the coherent phonon generation, two mechanisms have been invoked in the phenomenological analyses. One is the impulsively stimulated Raman scattering induced by a virtual electronic excitation during the irradiation of the laser pulse. The other is the displacive excitation which occurs through real electronic excitations. We have shown that the time-dependent density functional theory includes both mechanisms in a unified way [2].

Recently, we have undertaken a new project for a first-principles description of later-solid interaction going beyond the dipole (spatially uniform) approximation. Here we note that there are two distinct spatial scales: macroscopic electromagnetic field whose spatial scale is characterized by a wavelength of laser pulse (micrometer) is much longer than the typical spatial scale of electron dynamics (nanometer). We thus need to develop a coupled Maxwell-TDDFT multiscale simulator. We would like to present the formalism and a status of our numerical calculations.

[1] G.F. Bertsch, J.-I. Iwata, A. Rubio, K. Yabana, Phys. Rev. B62, 7998 (2000).

[2] T. Otobe, M. Yamagiwa, J.-I. Iwata, K. Yabana, T. Nakatsukasa, G.F. Bertsch, Phys. Rev. B77, 165104 (2008).

[3] Y. Shinohara, K. Yabana, Y. Kawashita, J.-I. Iwata, T. Otobe, G.F. Bertsch, Phys. Rev. B82, 155110 (2010).

General Theory for the Ferroelectric Polarization Induced by Spin-Spiral Order

H. J. Xiang¹, E. J. Kan², Y. Zhang³, M.-H. Whangbo³, and X. G. Gong¹

¹*Key Laboratory of Computational Physical Sciences (Ministry of Education), and Department of Physics, Fudan University, Shanghai 200433, P. R. China*

²*Department of Applied Physics, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, P. R. China*

³*Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, USA*

The ferroelectric polarization of triangular-lattice antiferromagnets induced by helical spin-spiral order is not explained by any existing model of magnetic-order-driven ferroelectricity. We resolve this problem by developing a general theory for the ferroelectric polarization induced by spin-spiral order and then by evaluating the coefficients needed to specify the general theory on the basis of density functional calculations. Our theory [1] correctly describes the ferroelectricity of triangular-lattice antiferromagnets driven by helical spin-spiral order, and incorporates known models of magnetic-order-driven ferroelectricity as special cases.

[1] H. J. Xiang *et al.*, arXiv:1109.1328 (To be published in Phys. Rev. Lett.)

Novel mechanisms for multiferroicity and magnetoelectric effects in transition metal oxides

Kunihiko Yamauchi

¹*ISIR-SANKEN, Osaka University, Ibaraki, Osaka 567-0047, Japan*

Improper multiferroics are attractive multifunctional materials where magnetism and ferroelectricity are strongly coupled. They can be classified according to different driving forces, which primarily break the spatial inversion symmetry paving the way to ferroelectricity: (i) spin order, (ii) charge order and (iii) orbital order.

In the second group, while LuFe_2O_4 has emerged as a prototype for a long time, we show that ferroelectricity in magnetite Fe_3O_4 is driven by charge ordering from first-principles calculations; in the low-temperature insulating phase, the charge-ordering pattern in the Cc structure indeed lacks the inversion symmetry so as to induce the electric dipole which connects Fe^{2+} and Fe^{3+} sites [1,2]. Moreover, we also show that magnetoelectricity in charge-/orbital-ordered Fe_3O_4 is driven by the interplay between orbital-order and on-site spin-orbit coupling [3]. The peculiar mechanism is associated with the spin-dependent p - d hybridization mechanism, which has been proposed as the driven force of magnetoelectricity in $\text{Ba}_2\text{CoGe}_2\text{O}_7$ [4].

Via a charge-constrained GGA+ U method that allows a precise control over the charge-ordering pattern, it is able to infer the ground state, by comparing the total energy of different charge-order configurations. By using the method, we propose iron fluoride $\text{K}_{0.6}\text{FeF}_3$ in the tungsten-bronze structure as a new candidate of charge-order induced ferroelectrics [5].

[1] M. Alexe et al., *Adv. Mater.*, **21**, 4452 (2009).

[2] K. Yamauchi, T. Fukushima, and S. Picozzi, *Phys. Rev. B* **79**, 212404 (2009).

[3] K. Yamauchi and S. Picozzi, arXiv:1010.1105.

[4] K. Yamauchi, P. Barone, and S. Picozzi, arXiv: 1103.3151, to be published in PRB.

[5] K. Yamauchi and S. Picozzi, *Phys. Rev. Lett.* 107202 (2010).

Electronic structure and correlation effects in iron-based superconductors

Takashi Miyake

¹*Nanosystem Research Institute, AIST, Tsukuba 305-8568, Japan*

²*Japan Science and Technology Agency*

The discovery of iron-based superconductors LaFePO and LaFeAsO_{1-x}F_x stimulated extensive works to clarify the origin and character of superconductivity, and also to search for new superconductors. It has been known from the early stage that their transition temperatures are strongly correlated with the geometry of the FeAs₄ tetrahedron. In order to clarify how the geometry affects the electronic structure, we have performed the LDA calculation of a recently synthesized superconductor Ca₄Al₂O_{6-y}Fe₂As₂ [1], which is characterized by the smallest bond angle, α , among the iron-pnictide superconductors. We found that the topology of the Fermi surfaces is different from that in LaFeAsO. As α increases, the xy state is pulled up. Eventually bands are rearranged, and the number of the Fermi surfaces changes around the Γ point. Analysis using Wannier functions will be given.

Another issue is electron correlation effect. Our cRPA calculation shows that the electron correlation is stronger when the anion atom height is large [2]. In particular, the Hubbard U in FeSe is substantially larger than that in LaFeAsO. We performed the LDA+DMFT calculations and found that LaFeAsO is moderately correlated [3], whereas the effective mass is significantly heavier in FeSe [4]. The spectral function of FeSe has a satellite at ~ 1.2 eV below the Fermi level, which can be regarded as a lower Hubbard band. These results show that correlation effects are strongly material dependent in iron-based superconductors.

[1] T. Miyake, T. Kosugi, S. Ishibashi and K. Terakura, JPSJ **79**, 123713 (2010).

[2] T. Miyake, K. Nakamura, R. Arita and M. Imada, JPSJ **79**, 044705 (2010).

[3] M. Aichhorn et al., PRB **80**, 085101 (2009).

[4] M. Aichhorn et al., PRB **82**, 064504 (2010).

Orbital features in electronic and magnetic properties of iron pnictides and chalcogenides

Hyoung Joon Choi

Department of Physics, Yonsei University, Seoul 120-749, Republic of Korea

<http://web.yonsei.ac.kr/choi>

Based on the density functional theory, we study electronic and magnetic properties of LnFeAsO ($\text{Ln}=\text{La, Ce, Pr, Nd, Sm, and Gd}$) as a function of Fe magnetic moment, and $\text{FeTe}_{1-x}\text{Se}_x$ and $\text{FeTe}_{1-x}\text{S}_x$ with virtual crystal approximation. For LnFeAsO , we predict the magnetic crossover from low-Fe-moment d_{xy} phase to high-Fe-moment d_{yz} phase at critical Fe magnetic moments depending on materials. This feature originates from competition between itinerant magnetism and local-moment magnetism, suggesting close relationship of Fermi-surface nesting, magnetic ordering, and superconductivity in the materials. For $\text{FeTe}_{1-x}\text{Se}_x$ and $\text{FeTe}_{1-x}\text{S}_x$, our results on the stability of single- and double-stripe-type antiferromagnetic (AFM) orderings show that the AFM ordering changes at $x = 0.24$ in $\text{FeTe}_{1-x}\text{Se}_x$ and at $x = 0.16$ in $\text{FeTe}_{1-x}\text{S}_x$. When x is small, double-stripe-type AFM ordering is more stable, but when x is large, single-stripe-type AFM ordering is more stable. These critical concentrations for change in AFM ordering are close to the on-set concentrations of Se and S doping for bulk superconductivity observed in experiments, suggesting that stability of the single-stripe-type AFM ordering is closely related to the occurrence of the superconductivity. This work was supported by NRF of Korea (Grant Nos. 2009-0081204 and 2011-0018306). Computational resources have been provided by KISTI Supercomputing Center (Project No. KSC-2011-C3-05).

Order-N electron transport calculations for ballistic, diffusive and polaron transport regimes

Hiroyuki Ishii¹, Nobuhiko Kobayashi¹, and Kenji Hirose²

¹*Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*

²*Green Innovation Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan*

Recent advances in nanoscience and nanotechnology have made it possible to fabricate electron devices from various kinds of materials controlled in atomic scale. For example, these include silicon nanowires, carbon nanotubes, graphenes, organic semiconductors, and molecular wires. In general, the electron transport properties are changed by atomic configuration of these materials and external condition such as temperature. Especially, around room temperature, the electron-phonon coupling effect on the transport is very important and a serious problem. The understanding of transport properties of materials strongly modified by (electron-phonon mediated) time-dependent structural changes has become a great theoretical challenge.

We have investigated the transport properties using an order-N transport calculation methodology called as “Time-Dependent Wave-Packet Diffusion (TD-WPD) method” [1]. This method computes quantum-mechanically the wave-packet dynamics for various huge systems with up to 10^8 atoms, which enables me to treat electron transport problems from classical diffusive regime to quantum ballistic regime. In the TD-WPD methodology, to consider the electron-phonon coupling effect on the transport, we combine the wave-packet dynamics with the molecular dynamics. As the results, we can describe the electron motion in time-dependent structural change due to the phonon vibrations. We evaluate the diffusion coefficients of electrons and then obtain the conductivity, mean free path, and carrier mobility within the Kubo formula.

Applying the present TD-WPD method to micron-long CNTs, we clarified the crossover from quantum ballistic to classical diffusive transport properties of the CNTs. Although the CNTs and graphenes are expected as quantum-device and high-mobility materials, the recent organic molecular semiconductors also attract attentions because of their flexibility. In the organic semiconductors, carriers induce the drastic lattice deformation, which is called as polaron state. Therefore, the transport mechanism of organic semiconductors is very different from that of CNTs. The transport mechanism of organic semiconductors has never been clarified yet from the atomistic viewpoint. We take the polaron effects into the TD-WPD methodology and evaluate the temperature-dependence of mobility of organic semiconductors.

I will talk about these results in my presentation.

[1] H. Ishii, N. Kobayashi, K. Hirose, Phys. Rev. B, **82** 085435 (2010).

Quantum transport and quantum information processing on single molecular junctions from first principles

Tomofumi Tada

Department of Materials Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Nuclear spins are a promising candidate for quantum information processing because of the long coherence. The observation and operation of nuclear spins in molecules in the liquid state were reported by Vandersypen and co-workers in 2001 [1], and a factorization using nuclear magnetic resonance (NMR) was demonstrated successfully, showing the enormous potential in quantum information technology. However, in the liquid state, the observed results are averaged values for a large amount of nuclear spins, resulting in the difficulties for the development of the NMR system in terms of initialization and scalability. If the observation and operation of a single nuclear spin are possible, the nuclear spin system will promote the further development for qubit systems based on nuclear spins.

A solid state system composed of a nuclear spin array supported by single molecular junctions (see Fig. 1(a)) is thus an attractive system for a nuclear-qubit system. The high self-assembling property of molecules on substrate will be necessary for the high scalability required in quantum computation. In this study, we theoretically investigated the possibilities of the observation and operation of a single nuclear spin (proton qubit) connected to source/drain electrodes, and found that the observation and operation of a single nuclear spin become feasible by means of the switching of the hyperfine interactions between nuclear and electronic spins, which is triggered by resonant tunneling through the nuclear qubit [2]. Figure 1(b) shows the relaxation times T_1 of the nuclear spin of proton in Pd/H₂/Pd as a function of the Fermi level shift ΔE_F . The resonant tunneling at the negative shift of the Fermi level enhances the electron density on the proton, resulting in the enhancement of the hyperfine interaction and fast relaxations (~ 10 s), whereas reduced electron density caused by the OFF-resonant tunneling at the positive shift of the Fermi level leads to the extremely slow relaxations ($\sim 10^4$ s). That is, the relaxation of a single proton spin in the nano-junction is tunable by the Fermi level shift (i.e., gate bias applications) through the enhanced/suppressed hyperfine interactions [2]. The dynamics of nuclear spin is thus clearly correlated with tunneling electrons, and we investigated electron transport in more complicated single molecular junctions [3,4].

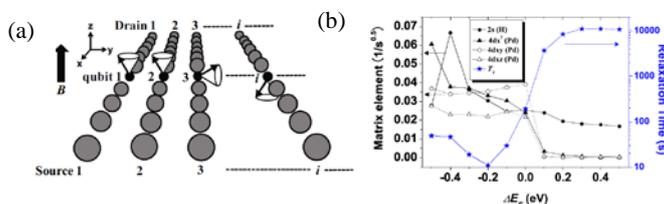


Fig. 1: (a) Solid state qubit system composed of nuclear spins and source/drain electrodes. (b) Computed relaxation times and significant matrix elements in hyperfine interactions as a function of the Fermi level shift ΔE_F .

[1] L. M. K. Vandersypen et. al, *Nature* **414**, 883 (2001).

[2] T. Tada, *Phys. Lett. A* **372**, 6690 (2008).

[3] M. Kiguchi et al., *Angew. Chem. Int. Ed.* **50**, 5708 (2011).

[4] T. Tada, T. Yamamoto, and S. Watanabe, *Theor. Chem. Acc.*, in press.

Beyond DFT with quantum Monte Carlo and wavefunction-based quantum chemistry

Mike Gillan^{1,2}

¹*London Centre for Nanotechnology, UCL, 17 – 19 Gordon Street, London WC1H 0AH, UK*

²*Thomas Young Centre at UCL, 17 – 19 Gordon Street, London WC1H 0AH, UK*

Over the past 20 years, density functional theory (DFT) has come to dominate the computational study of materials on the atomic scale, and is now used across a vast range of fields, including surface and interface physics and chemistry, structural and electronic defects in materials, solids and liquids at extreme conditions, metallurgy, biomolecular science, and many others. Nevertheless, it is well known that there are important kinds of problems for which the predictive power of DFT is sometimes too poor for practical purposes. Examples include the surface formation energy of materials, the adsorption and reaction energies of molecules on surfaces, and the many molecular solids and liquids (including water) where van der Waals forces play an important role. In cases like this, there is an urgent need for accurate benchmark calculations, which can be used to calibrate and “tune” DFT approximations. There are two kinds of technique available for generating such benchmarks: quantum Monte Carlo (QMC) and the wavefunction-based methods of traditional quantum chemistry, such as second-order Møller-Plesset and the coupled-cluster hierarchy. I will show how in some cases QMC and quantum chemistry can work closely together to produce energy benchmarks of very high accuracy for surface formation energies [1-3] and surface adsorption energies [4]. Preliminary QMC and quantum-chemistry benchmarking [5] for random thermal samples of water clusters will also be summarized.

[1] S. J. Binnie, E. Sola, D. Alfè and M. J. Gillan, *Molec. Simulation*, 35, 609 (2009).

[2] S. J. Nolan, M. J. Gillan, D. Alfè, N. L. Allan and F. R. Manby, *Phys. Rev. B*, 80, 165109 (2009).

[3] S. J. Binnie, S. J. Nolan, N. D. Drummond, D. Alfè, N. L. Allan, F. R. Manby and M. J. Gillan, *Phys. Rev. B*, 82, 165431 (2010).

[4] S. J. Binnie, B. Paulus, D. Alfè and M. J. Gillan, in preparation.

[5] M. J. Gillan, F. R. Manby, D. Alfè, A. Bartók-Pártay and G. Csányi, unpublished.

Systematically improvable optimized atomic basis sets for *ab initio* calculations

Lixin He

Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei, Anhui, 230026

I will introduce a unique scheme to construct fully optimized atomic basis sets for density-functional calculations [1]. In this scheme, the shapes of the atomic radial functions are optimized by minimizing the *spillage* of the wave functions between the atomic orbital calculations and the converged plane wave calculations for dimer systems. The quality of the bases can be systematically improved by increasing the size of the bases within the same framework, where the spillage can be used as the criterion of convergence. The scheme is easy to implement and very flexible. We have done extensive tests of this scheme for wide variety of systems. The results show that the obtained atomic basis sets are very satisfactory for both accuracy and transferability. I will further show that this scheme can be easily revised to be an efficient scheme for accurate electronic structure interpolations [2].

[1] M Chen, G-C Guo, and L He, J. Phys.: Condens. Matter **22**, 445501 (2010).

[2] M Chen, G-C Guo, and L He, J. Phys.: Condens. Matter **23**, 325501 (2011).

First-principles calculations of large super cells and nanoclusters based on symmetrized basis

Yia-Chung Chang¹

¹*Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan*

We illustrate the use of basis functions to compute the electronic states and optical properties of a large supercells and nanoclusters with high point group symmetry. We show that the use of symmetrized basis can substantially reduce the computation time and memory by one or two orders of magnitude. Examples for defects (vacancies and donor-vacancy pair) in compound semiconductors studied with a full-potential symmetrized linearized augmented Slater-type orbital (LASTO) code [1,2] and optical excitation spectra of semiconductors [3] and nanostructures [4] are presented. The advantages of using LASTO basis for studies of optical excitations and transport will also be discussed.

[1] J. W. Davenport, Phys. Rev. B **29**, 2896 (1984).

[2] Y.-C. Chang, R. B. James, and J. Davenport, Phys. Rev. B **73**, 035211 (2006).

[3] J. J. Yoon, T. J. Kim, Y. W. Jung, D. E. Aspnes, Y. D. Kim, H. J. Kim, Y. C. Chang, S. H. Shin, and J. D. Song, Appl. Phys. Lett., **97**, 111902 (2010); H. J. Kim, Z. Ning, and Y.-C. Chang (unpublished).

[4] G. Qian, Z. Ning, and Y.-C. Chang (unpublished).

Low-Order Scaling Density Functional Methods Based on Quantum Nearsightedness

Taisuke Ozaki

*Research Center for Integrated Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan*

Physical quantities such as total energy in the density functional theory (DFT) can be expressed by nearsighted variables: density matrix and Wannier function. The nearsightedness in describing physical quantities may enable us to develop efficient electronic structure methods of which computational cost scales in a lower order compared to conventional methods. As such practical methodological developments, we present an approximate $O(N)$ Krylov subspace method [1] and a numerically exact low-order scaling method based on a contour integration and a selected inversion algorithm [2,3] as Kohn-Shan eigenvalue solver. It is also shown that an *exact* exchange functional, which is nearly self-interaction free and possesses the correct asymptotic behavior of the exchange potential, can be developed by introducing a range-separation of exchange hole based on the nearsightedness [4]. The methodological basis, its implementation to the OpenMX code [5-7], and recent applications [8,9] will be discussed.

- [1] T. Ozaki, Phys. Rev. B 74, 245101 (2006).
- [2] T. Ozaki, Phys. Rev. B 75, 035123 (2007).
- [3] T. Ozaki, Phys. Rev. B 82, 075131 (2010).
- [4] M. Toyoda and T. Ozaki, Phys. Rev. A 83, 032515 (2011).
- [5] T. Ozaki, Phys. Rev. B 67, 155108 (2003).
- [6] T. Ozaki and H. Kino, Phys. Rev. B 72, 045121 (2005).
- [7] <http://www.openmx-square.org>
- [8] T. Ohwaki, M. Otani, T. Ikeshoji, and T. Ozaki, in progress.
- [9] H. Sawada and T. Ozaki, in progress.