

***Kobe workshop for material design
on strongly correlated electrons in
molecules and materials
Program***

Kobe workshop for material design on strongly correlated electrons in molecules and materials

All talks are in the 1st floor seminar room: C111/C112

K Computer Presentation: 6th floor visitor room

Program

Wednesday, February 17, 2016

9:30-10:00	Registration	
10:05-10:10	Opening Remarks	
10:10-10:55	<u>Paul W. Ayers</u> , <i>Department of Chemistry and Chemical Biology, McMaster University</i> Methods for strong correlation from the wavefunction forms of exactly solvable models	Chair: Mario Piris
10:55-11:40	<u>Wataru Uemura</u> , <i>Institute for Solid State Physics, University of Tokyo</i> Configuration interaction with antisymmetrized geminal powers	
11:40-11:50	Photo	
11:40-13:10	Lunch	
13:10-13:55	<u>Seiichiro Ten-no</u> , <i>Graduate School of System Informatics, Kobe University</i> TBA	Chair: Paul W. Ayers
13:55-14:40	<u>Hiroyuki Nakashima</u> , <i>Quantum Chemistry Research Institute</i> Solving the Schrödinger equations of interstellar molecules	
14:40-15:10	Break	
15:10-15:55	<u>Mario Piris</u> , <i>Kimika Fakultatea, Euskal Herriko Unibertsitatea</i> Natural Orbital Functional Theory: an alternative to DFT	Chair: Seiichiro Tenno
15:55-16:40	<u>Maho Nakata</u> , <i>Advanced Center for Computing and Communication, RIKEN</i> The PubChemQC Project: a large chemical database from the first principle calculations	

Thursday, February 18, 2016

9:50-10:35	<u>Sergei Manzhos</u> , <i>Department of Mechanical Engineering, National University of Singapore</i> Large-scale density functional based methods from the perspective of computational materials science	Chair: Annika Bande
10:35-11:20	<u>Jeng-Da Chai</u> , <i>Department of Physics, National Taiwan University</i> TAO-DFT and its applications to zigzag graphene nanoribbons	
11:30-12:00	K Computer Presentation/Photo	
12:00-13:20	Lunch	
13:20-14:05	<u>Annika Bande</u> , <i>Institute of Methods for Material Development and Joint Ultrafast Dynamics Lab JULiq in Solutions and at Interfaces, Freien Universität Berlin</i> Electron Dynamics of Ultrafast Energy Transfer Processes in Quantum Dots	Chair: Sergei Manzhos
14:05-14:50	<u>Juan Ignacio Rodriguez Hernandez</u> , <i>Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional</i> Theoretical study on the structural, electronic and optical properties of nanostructures used in organic solar cells	
14:50-15:05	Break	
15:05-15:50	<u>Aron Beekman</u> , <i>Department of Physics & Research and Education Center for Natural Sciences, Keio University</i> Duality methods in quantum melting phase transitions	Chair: TBA
15:50-16:35	<u>Hiroshi Shinaoka</u> , <i>Department of Physics, Saitama University</i> Relativistic first-principles study of pyrochlore oxides	
16:35-17:20	<u>Mohammad Khazaei</u> , <i>Computational Materials Science Unit, National Institute for Materials Science</i> Electronic structures of MAX phases and MXenes	
17:20-17:25	Closing Remarks	

Methods for strong correlation from the wavefunction forms of exactly solvable models

Paul W. Ayers

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Modeling strong correlation is so difficult that theorists often settle for *qualitative* descriptions of strongly-correlated substances (e.g. heavy-fermion materials, high-temperature superconductors). These qualitative approaches are typically based on model Hamiltonians for which the Schrödinger equation can be solved exactly via the Bethe ansatz. In this way one ensures that at least the key qualitative features of the system are all captured. We recently realized that wavefunction forms inspired by algebraic models could also be used to obtain *quantitative* accuracy, while maintaining the computational feasibility associated with the simplified model systems.

Configuration interaction with antisymmetrized geminal powers

Wataru Uemura

ISSP, The University of Tokyo

In this talk, we introduce our recent results for the tensor decomposition description of many electron systems, that can efficiently obtain the ground state energy of the system with high accuracy. We have reported the symmetric tensor decomposition version of the theory that accurately reproduce the potential curves of H₂, He₂ and LiH [1]. We further extended this scheme and found a formalism based on the linear combination of antisymmetrized geminal powers. We applied this formalism to the Hubbard model and the H₂O molecule and obtained highly accurate ground state energy [2]. The algorithm works on the computational scaling of the fifth power of the number of electrons and can be regarded as a promising candidate for high precision electronic structure calculation of further larger systems.

References

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TBA

Solving the Schrödinger equations of interstellar molecules

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Schrödinger equation governs most of phenomena in molecular science including astrochemistry. For interstellar molecules, although small atoms and molecules are rather main species, precise quantum mechanical calculations beyond spectroscopic accuracy (cm⁻¹) are often required to distinguish the target species from astronomical interstellar bands or to treat systems in extreme environments in space (like very low-temperatures and/or strong magnetic fields etc.), where experimental studies are generally difficult and even impossible. For the objective of exactly solving the Schrödinger equation, the free complement (FC) method was proposed [1] and extended to the relativistic Dirac equation [2]. We have applied it to the following situations that are significant in the interstellar space: the excited states and their spectra, non-Born-Oppenheimer (non-BO) calculations that include quantum mechanical effects of nuclear motions [3], solving the relativistic Dirac equation [2], and atoms and molecules in extreme environments such as under strong magnetic fields [4].

For example, the non-BO calculations are significant for the hydrogen-related compounds. They can provide rotational vibrational states including all the quantum effects of electron-nuclear motions and, therefore, their theoretical database are directly comparable with the astronomical observation and/or the low-temperature experimental result. We also proposed a new method to describe an analytical potential curve from the non-BO wave functions [5] although one may think that the non-BO calculations lose the property of potential curve that is essentially significant for discussing chemical reactions. This method might rather overcome some problems when drawing the ordinary potential curve on the BO approximation and would become a new analysis method for understanding complicated chemical reactions.

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Natural Orbital Functional Theory: an alternative to DFT

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Abstract. Since the Hamiltonian operator contains only one- and two-electron operators, the energy of an electron system can be determined exactly from the knowledge of the one- and two-particle reduced density matrices (1- and 2-RDMs). In 1974, Gilbert proved for the 1-RDMs an analogous theorem to the Hohenberg-Kohn theorem for the density. Accordingly, one can employ the exact functional with an approximate 2-RDM that is built from the 1-RDM using a reconstruction functional. The major advantage of a 1-RDM formulation is that the kinetic energy is explicitly constructed and does not require a functional. The 1-RDM functional is called Natural Orbital Functional (NOF) [1] when it is based upon the spectral expansion of the 1-RDM. An approximate reconstruction, in terms of the diagonal 1-RDM, has been achieved by imposing necessary N-representability conditions on the 2-RDM [2]. Appropriate forms of the two-particle cumulant have led to different implementations [3], being the most successful the PNOF5 [4] and its extended version PNOF5e [5]. On the other hand, antisymmetrized product of strongly orthogonal geminals (APSG) with the expansion coefficients explicitly expressed by means of the occupation numbers have been used to generate these NOFs [6], which demonstrates strictly the Nrepresentability, size-extensivity and size-consistency of the functionals. Moreover, it opens the possibility of using a perturbation theory to recover the missing dynamic correlation. Recently [7], an interacting-pair model has been proposed to attain a new NOF: PNOF6. The new approach belongs to the JKL-only family of functionals. PNOF6 is superior to its predecessor PNOF5, which is an independent-pair approach. The functional is able to treat properly the static correlation and recover an important part of dynamic correlation, there by putting together the advantages of the other members of this functional series.

In this presentation, the theory will be outlined and some challenging examples are presented including the bonding conundrum in the C₂ dimer [8]. Special emphasis will be done on strong correlated problems. The exact and approximate energies provided by 8 known NOFs in the singlet state of the 4e- harmonium atom will be analyzed [9]. It will be shown that PNOF6 exhibits the most consistent behavior along all confinement regimes studied.

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The PubChemQC Project: a large chemical database from the first principle calculations

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Abstract. In this research, we have been constructing a large database of molecules by *ab initio* calculations. Currently, we have over 3 million entries of 6-31G* B3LYP optimized geometries and 2.6 million entries for ten excited states by 6-31+G* TDDFT calculations. To calculate molecules, we only refer the InChI (International Chemical Identifier) representation of chemical formula by the International Union of Pure and Applied Chemistry (IUPAC), thus, no reference to experimental data. These results are open to public at <http://pubchemqc.riken.jp/>. The molecular data have been taken from the PubChem Project (<http://pubchem.ncbi.nlm.nih.gov/>), which is one of the largest in the world (approximately 63 million molecules are listed) and free (public domain) database. Our final goal is, using these data, to develop a molecular search engine or molecular expert system to find molecules, which have desired properties.

Large-scale density functional based methods from the perspective of computational materials science

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Density functional theory (DFT, in the Kohn-Sham formulation) has dominated the field of ab initio modeling of materials for the past two decades. In spite of its convenience, DFT calculations can only be *routinely* done on small, idealized model systems containing $<10^3$ atoms for most simulations. Likewise, ab initio molecular dynamics simulations are also impractical for time scales at which most phenomena are observed. This significantly limits explanatory and predictive power of ab initio simulations *regardless of how accurate the calculation is*: from microstructure of alloys to reactions involving biomolecules, one can argue that most practically important phenomena cannot be modelled *directly*.

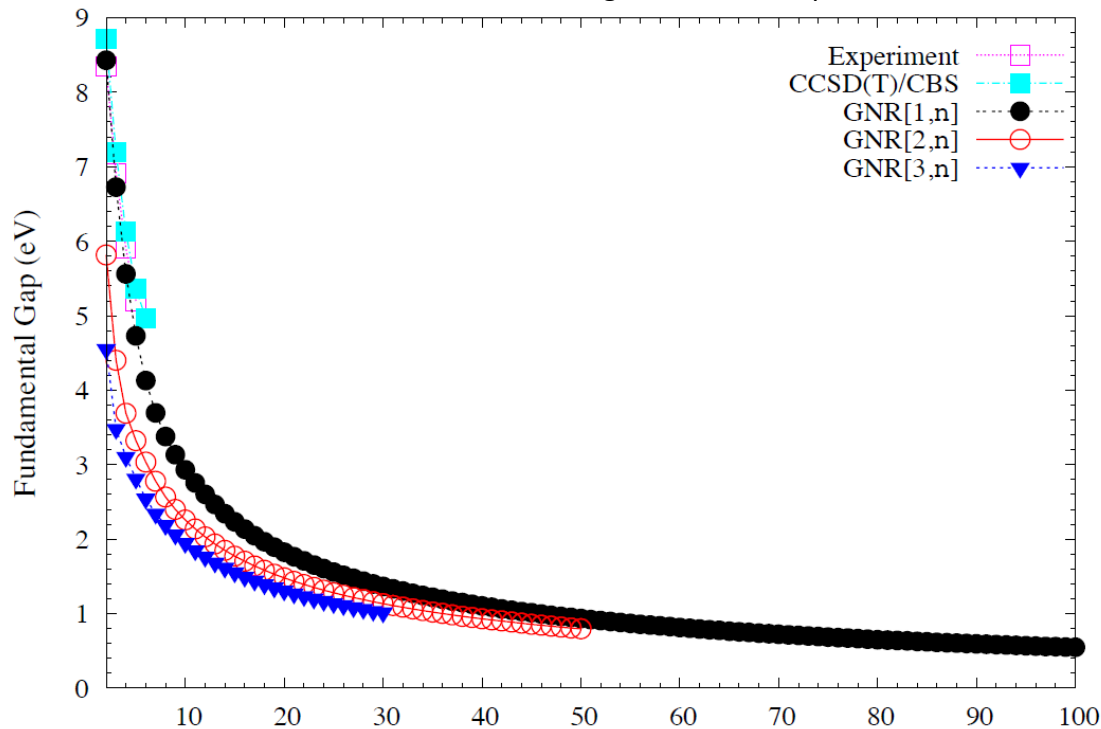
In this talk, I will review my group's experience with large-scale density functional based methods used to model different classes of materials: density-functional tight binding (DFTB, offering ~ 3 orders of magnitude cpu cost reduction vs. DFT) for organic materials and organic-inorganic interfaces and orbital-free DFT (OF-DFT, offering a near-linear scaling with system size) for metals. I will show that DFTB with existing parameterizations can provide ab initio accuracy for organic material, both covalent and vdW-bound. When modeling organic-inorganic interfaces where band alignment is important, I will present examples of systems where DFTB fails and where, on the contrary, it performs better than GGA DFT (which is still the most practical DFT approximation for large systems, as opposed to the cpu-costly hybrid functionals). I will present an approach to alleviate one of the bottlenecks of OF-DFT for periodic systems, namely the absence of accurate local pseudopotentials, and will argue that OF-DFT need not be less accurate than Kohn-Sham DFT.

TAO-DFT and Its Applications to zigzag graphene nanoribbons

Jeng-Da Chai

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In this talk, I will briefly describe the formulation of our recently proposed thermally-assisted-occupation density functional theory (TAO-DFT) [1], the density functional approximations to TAO-DFT [2], and the electronic properties of zigzag graphene nanoribbons (ZGNRs) studied by TAO-DFT [3]. In contrast to Kohn-Sham DFT, TAO-DFT is a DFT with fractional orbital occupations given by the Fermi-Dirac distribution (controlled by a fictitious temperature), for the study of large ground-state systems with strong static correlation effects. Relative to TAO-LDA (i.e., the local density approximation to TAO-DFT), TAO-GGAs (i.e., the generalized-gradient approximations to TAO-DFT) are significantly superior for a wide range of applications, such as thermochemistry, kinetics, and reaction energies. For noncovalent interactions, TAO-GGAs with empirical dispersion corrections are shown to yield excellent performance. Due to its computational efficiency for systems with strong static correlation effects, TAO-LDA is applied to study the electronic properties of hydrogen-terminated ZGNRs with different widths and lengths, which is very challenging for conventional electronic structure methods. Some interesting results will be presented in this talk.



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Electron dynamics of ultrafast energy transfer processes in quantum dots

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The elementary physical process of interatomic Coulombic decay (ICD)¹ and the interatomic Coulombic electron capture (ICEC)² are recognized as an ultrafast energy transfer process between atoms and molecules induced by long-range electron correlation. A few years ago we have shown that they are possible when electrons are confined in an array of two general, non-infinite binding potentials commonly used to model quantum dots (QDs).³ In ICD one electron bound to the left QD is radiatively excited to a higher, resonance state, after which it deexcites by transferring its energy to the neighboring QD, from which a second electron is emitted. In ICEC electron release from one QD happens upon electron capture by the other QD.

Both processes were studied by means of highly accurate electron dynamics calculations with an antisymmetrized version of the multiconfiguration time-dependent Hartree method.⁴ Here we present the effect of the control factors geometry, laser, and phonons on the processes with view on experimental realizations.

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Theoretical study on the structural, electronic and optical properties of nanostructures used in organic solar cells

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To try to understand the molecular structure and the electronic properties of a blend of the polymer poly(3-hexylthiophene) (P3HT) and the [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), which is used in one of the most efficient bulk-heterojunction organic solar cell, we performed a DFT-TDDFT-QTAIM theoretical study of the P3HT-PCBM dimer. A dispersion-corrected exchange-correlation potential was used to afford for the long-range van der Waals dispersion interactions in obtaining realistic structures. From TDDFT calculations it was determined that the maximum absorption intensity of the P3HT-PCBM dimer undergoes a blue-shift of about 80 nm with respect to the isolated P3HT oligomer in qualitative agreement with the experimental facts. It was also determined that that blue-shift can be attributed to distortions in the P3HT oligomer upon dimer formation and is not caused by electronic interactions between the P3HT-PCBM. The reduction of the absorption intensity in the red part of such spectrum can be attributed to both distortions of P3HT and interaction of it with PCBM. This result does not depend on the choice of exchange-correlation functional and is in qualitative agreement with experiments on the corresponding solid-state films.

Duality methods in quantum melting phase transitions

Aron Beekman

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One way to tackle the problem of analyzing a strongly-correlated system is to map it onto a weakly-correlated one, using a so-called strong/weak duality, following Kramers and Wannier who did this for the Ising model. Starting out from a maximally ordered state with weak correlations, turning up the interaction strength will drive a quantum phase transition by proliferation (unbinding) of topological defects, such as vortices, dislocations etc. This is fully captured in an effective disorder-parameter theory. I will present an overview of recent results on the superfluid/superconductor-insulator transition and on quantum liquid crystals. We predict several new phases of matter, featuring for instance vortex lines of quantized currents and rotational Nambu-Goldstone modes.

Relativistic first-principles study of transition metal oxides

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Fascinating phenomena are induced by the competition of strong electron correlations and spin-orbit coupling in $4d$ and $5d$ transition metal oxides. The pyrochlore iridates $A2\text{Ir}2\text{O}7$ ($A=\text{Pr}$, Nd , Y , *etc.*) are an ideal system to study such phenomena because their magnetic and electronic states can be tuned by chemical substitution, pressure, and temperature. A pioneering local density approximation (LDA)+ U study for this compound found a Weyl semimetal as the possible ground state of some compounds in this series [1]. Although this stimulated further theoretical and experimental studies, the role of strong correlations in the phase diagram remains to be clarified.

In this talk, we study strong correlation effects in the prototype compound $\text{Y}2\text{Ir}2\text{O}7$ using the state-of-the-art first-principles method: the local density approximation and dynamical meanfield theory (LDA+DMFT) [2]. We map out the phase diagram in the space of temperature, onsite Coulomb repulsion U , and filling. Consistent with experiments, we find that an all-in/all-out ordered insulating phase is stable for realistic values of U . We reveal the importance of the hybridization between $j_{\text{eff}}=1/2$ and $j_{\text{eff}}=3/2$ states under the Coulomb interaction and trigonal crystal field. We demonstrate a substantial band narrowing in the paramagnetic metallic phase and non-Fermi liquid behavior in the electron/hole doped system originating from long-lived quasi-spin moments induced by nearly flat bands. The Weyl semimetal phase gives way to a direct transition between the paramagnetic metal and the all-in/all-out ordered insulating phase. Recently, it was reported that the magnetic transition temperature shows a non-monotonic pressure dependence for $\text{Eu}2\text{Ir}2\text{O}7$ under hydrostatic pressure [3]. Our phase diagram is in good agreement with this experimental result. We also discuss possible applications of our method to films and super-lattice structures of pyrochlore iridates.

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Electronic structures of MAX phases and MXenes

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Recently, some of the layered MAX phases — $Mn+1AX_n$ systems, where $n = 1, 2,$ or 3 , "M" is an early transition metal, "A" is A group elements, mostly groups 13 and 14 elements, and "X" is carbon and/or nitrogen — have been exfoliated into twodimensional single- and multi-layers, so-called MXenes [1]. MAX phases are metallic systems [2]. However, our calculations exhibited that that upon appropriate functionalization by F, OH, and O groups, some of the exfoliated 2D-MXenes become semiconductor [3]. In this presentation, I will give an overview of the electronic structures of MAX phases and MXenes [4]. Then, I will discuss how different surface functionalizations affect the work function properties and generate new surface states on MXenes. At the end, as an application the results of thermoelectric properties (Seebeck, electrical conductivity, and power factor) of MXenes are presented [5].

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