

## O 39: Focused session: Frontiers of electronic structure theory: Strong correlations from first principles III (jointly with TT)

Time: Wednesday 10:30–13:15

Location: HE 101

O 39.1 Wed 10:30 HE 101

### Reduced effective spin-orbital degeneracy and spin-orbital ordering in paramagnetic transition metal oxides:

**Sr<sub>2</sub>IrO<sub>4</sub> vs. Sr<sub>2</sub>RhO<sub>4</sub>** — ●CYRIL MARTINS<sup>1,2</sup>, MARKUS AICHHORN<sup>1,3</sup>, LOÏG VAUGIER<sup>1</sup>, and SILKE BIERMANN<sup>1,2</sup> — <sup>1</sup>Centre de Physique Théorique, Ecole Polytechnique, CNRS, 91128 Palaiseau Cedex, France. — <sup>2</sup>Japan Science and Technology Agency, CREST, Kawaguchi 332-0012, Japan. — <sup>3</sup>Institute of Theoretical and Computational Physics, TU Graz, Petersgasse 16, Graz, Austria.

We discuss the notions of spin-orbital polarization and ordering in paramagnetic materials, and address their consequences in transition metal oxides. Extending the combined density functional and dynamical mean field theory scheme to the case of materials with large spin-orbit interactions, we investigate the electronic excitations of the paramagnetic phases of Sr<sub>2</sub>IrO<sub>4</sub> and Sr<sub>2</sub>RhO<sub>4</sub>. We show that the interplay of spin-orbit interactions, structural distortions and Coulomb interactions suppresses spin-orbital fluctuations. As a result, the room temperature phase of Sr<sub>2</sub>IrO<sub>4</sub> is a paramagnetic spin-orbitally ordered Mott insulator. In Sr<sub>2</sub>RhO<sub>4</sub>, the effective spin-orbital degeneracy is reduced, but the material remains metallic, due to both, smaller spin-orbit and smaller Coulomb interactions. We find excellent agreement of our *ab-initio* calculations for Sr<sub>2</sub>RhO<sub>4</sub> with angle-resolved photoemission, and make predictions for spectra of the paramagnetic phase of Sr<sub>2</sub>IrO<sub>4</sub>.

O 39.2 Wed 10:45 HE 101

### *Ab initio* determination of excitation energies and magnetic couplings in correlated, quasi two-dimensional iridates —

●VAMSHI KATUKURI<sup>1</sup>, HERMANN STOLL<sup>2</sup>, JEROEN VAN DEN BRINK<sup>1</sup>, and LIVIU HOZOI<sup>1</sup> — <sup>1</sup>Institute for Theoretical Solid State Physics, IFW Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany — <sup>2</sup>Institute for Theoretical Chemistry, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

Using many-body quantum-chemical techniques, we compare the electronic structure of two layered  $j=1/2$  Ir  $5d^5$  oxides, Sr<sub>2</sub>IrO<sub>4</sub> and Ba<sub>2</sub>IrO<sub>4</sub>. Multi-orbital and multiplet physics, spin-orbit interactions and  $O\ 2p$  to Ir  $5d$  charge-transfer effects are all treated on equal footing, fully *ab initio*. Our calculations provide valuable complementary information to hybrid schemes based on density-functional theory and dynamical mean-field theory. In particular, for Sr<sub>2</sub>IrO<sub>4</sub>, the computed magnetic constant ( $J$ ),  $d-d$  and charge-transfer excitation energies show good agreement with recent resonant inelastic x-ray scattering and optical measurements. For Ba<sub>2</sub>IrO<sub>4</sub>, we find a  $J$  that is even somewhat larger, which renders it roughly a factor 2-3 lower than the  $J$ 's in typical quasi 2D cuprates. This might in itself be encouraging for a scenario of magnetic mediated super-conductivity in doped iridates.

O 39.3 Wed 11:00 HE 101

### First-principles study of electronic structure and magnetism of CaIrO<sub>3</sub> —

●ALASKA SUBEDI — Max Planck Institute for Solid State Research, Stuttgart, Germany

Recent experiments by Ohgushi and co-workers show that post-perovskite CaIrO<sub>3</sub> is a Mott insulator in a  $J_{\text{eff}} = 1/2$  state.[1,2] I study the electronic structure and magnetism of post-perovskite CaIrO<sub>3</sub> using first principles calculations. The density functional calculations within the local density approximation without the combined effect of spin-orbit coupling and on-site Coulomb repulsion show the system to be metallic, which is in disagreement with the experimental evidences. However, when spin-orbit coupling is taken into account, the Ir  $t_{2g}$  bands split into fully-filled  $J_{\text{eff}} = 3/2$  bands and half-filled  $J_{\text{eff}} = 1/2$  bands. I find that spin-orbit coupling along with a modest on-site Coulomb repulsion opens a gap leading to a Mott insulating state. The ordering is antiferromagnetic along the  $c$ -axis with total moments aligned antiparallel along the  $c$ -axis and canted along the  $b$ -axis.

[1] K. Ohgushi, J.-I. Yamaura, H. Ohsumi, K. Sugimoto, S. Takeshita, A. Tokuda, H. Takagi, M. Takata, and T.-H. Arima, arXiv:1108.4523.

[2] K. Ohgushi, H. Gotou, T. Yagi, Y. Kiuchi, F. Sakai, and Y. Ueda, Phys. Rev. B **74**, 241104(R) (2006).

O 39.4 Wed 11:15 HE 101

### Interplay of Coulomb interactions and spin-orbit coupling in the bilayer Ruthenate Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> —

●MALTE BEHRMANN, CHRISTOPH PIEFKE, and FRANK LECHERMANN — 1. Institut für Theoretische Physik, Universität Hamburg

The combination of the local-density approximation to density functional theory with explicit many-body approaches has proven to be a powerful tool to investigate the problem of strong electronic correlations on a realistic level. The complex interplay of the effective dimensionality and the symmetry of the underlying crystal structure with the competition between the localized and the itinerant character of electrons is indeed giving rise to highly interesting physical phenomena in many modern materials, especially within the family of transition-metal oxides.

Here we want to discuss the intriguing interplay between rotational-invariant local Coulomb interactions and spin-orbit coupling for the case of the bilayer Ruthenate Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>. New results based on a generic realistic modeling of the correlated electronic structure will be presented. In this respect, also the intriguing metamagnetic behavior of Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> will be addressed.

O 39.5 Wed 11:30 HE 101

### Strong correlations enhanced by charge-ordering in highly doped cobaltates —

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Layered cobaltates represent a family of strongly correlated systems with quite unusual properties. In particular, they exhibit the strong mass and low-temperature-conductivity renormalization in the high-doping regime. We present an explanation for the puzzling spectral and transport properties of layered cobaltates close to the band-insulator limit, which relies on the key effect of charge ordering. Blocking a significant fraction of the lattice sites deeply modifies the electronic structure in a way that is shown to be quantitatively consistent with photoemission experiments. It also makes the system highly sensitive to interactions (especially to intersite ones), hence accounting for the strong correlations effects observed in this regime, such as the high effective mass and quasiparticle scattering rate. These conclusions are supported by a theoretical study of an extended Hubbard model with a realistic band structure on an effective kagome lattice.

O 39.6 Wed 11:45 HE 101

### Magnetic charge-ordered bad-metal ground state of nickelate superlattices —

DANILO PUGGIONI, ALESSIO FILIPPETTI, and ●VINCENZO FIORENTINI — Dept of Physics, U of Cagliari and CNR-IOM, Cagliari, Italy

Short-period strained LaNiO<sub>3</sub>/LaAlO<sub>3</sub> superlattices undergo paramagnetic-antiferromagnetic metal-“insulator” transitions at low temperature, with charge ordering signaled by spectral weight transfer and XAS line splitting. Further, DMFT calculations suggest that the Fermi surface may become a single hole-like cylinder similar to optimally-doped cuprates, quite unlike that of bulk LaNiO<sub>3</sub>.

We report *ab initio* self-interaction-corrected density functional calculations showing that these superlattices are antiferromagnetic and charge-ordered. Although not gap-insulating, they show a sharp pseudo-gap at the Fermi energy, a dc conductivity 2 orders of magnitude lower than in the paramagnetic phase, and a joint density of states for vertical transitions kicking in near the experimental charge gap. While the paramagnetic state has a cuprate-like Fermi surface, the ground-state antiferromagnetic phase has a reconstructed, underdoped-cuprate-like Fermi surface with both electron and hole-like small pockets, at points known as “nodal” and “antinodal” in cuprates. We thus predict that these superlattices should exhibit quantum oscillations in magnetic field.

O 39.7 Wed 12:00 HE 101

### Computing the magneto-electric coupling between atoms with numerous open-shells to experimental accuracy : YMnO<sub>3</sub>

— ●MARIE-BERNADETTE LEPETIT — CRISMAT UMR6508 CNRS-ENSICAEN, 6 bd Maréchal Juin, 14050 Caen, FRANCE

In strongly correlated systems the electron-electron repulsion between the Fermi level electrons is of larger magnitude than the kinetic energy. It results that the nature of the ground and the low-lying excited-states is thus fundamentally multi-configurational and single-determinant based methods (such as density functional theory) encounter difficulties in properly describing their electronic structure and more specifically their magnetic properties.

The multireference CAS+DDCI [1] and related LCAS+S [2] methods proved their high reliability and efficiency for accessing the local physics such as the magnetic exchange within experimental accuracy, however they cannot be used for systems involving more than one or two unpaired electrons per magnetic center. We will use a simple physical criterion in order to propose a new ab initio approach that overcomes this problem [3].

We used this new method to study the magneto-electric coupling in a prototypal magneto-electric system  $\text{YMnO}_3$  [4]. Indeed we were able to compute the magnetic exchange as a function of an applied electric field within experimental accuracy. The importance of the different microscopic contributions (piezzo-magnetic effects, spin-orbit coupling etc...) on the magneto-electric coupling will be discussed from the ab-initio results.

[1] J. Miralles, J. P. Daudey and R. Caballol, *Chem. Phys. Lett.* **198**, (1992) 555 ; V. M. García *et al.*, *Chem. Phys. Lett.* **238**, (1995) 222 ; V. M. García, M. Reguero and R. Caballol, *Theor. Chem. Acc.* **98**, (1997) 50.

[2] A. Gellé, M. L. Munzarová, M.B. Lepetit and F. Illas, *Phys. Rev. B* **68**, 125103 (2003) ; C J. Calzado, J. F. Sanz and J. P. Malrieu, *J. Chem. Phys.* **112**, 5158 (2002).

[3] A. Gellé, J. Varignon et M.-B. Lepetit, *EPL* **88** 37003 (2009).

[4] J. Varignon and M.-B. Lepetit, in preparation.

O 39.8 Wed 12:15 HE 101

**Electron conductivity of  $\text{Li}_2\text{O}_2$  in Li-air batteries** — ●JUAN MARÍA GARCÍA LASTRA and KRISTIAN THYGESSEN — Center for Atomic-scale Design. Technical University of Denmark.

The development of non-aqueous Li-air batteries in the late 90s and the rapidly growing demands for better and more sustainable methods for energy storage, have recently spurred a great deal of interest in the material  $\text{Li}_2\text{O}_2$ . The main limiting factor in the performance of reversible Li-air batteries, namely the large potential losses at realistic current densities, is believed to be related to poor intrinsic transport properties of  $\text{Li}_2\text{O}_2$  and/or the carbon-  $\text{Li}_2\text{O}_2$  interface.  $\text{Li}_2\text{O}_2$  is a wide-gap insulator material (4.9 eV gap) and thus is only able to transport electrons if it contains some kind of defect.  $\text{Li}^+$  ion vacancies have been detected by means of X-ray diffraction (XRD) and X-Ray Absorption Near Edge Spectroscopy (XANES) in  $\text{Li}_2\text{O}_2$  during the discharge of the Li-air batteries. These defects are believed to be the responsible for the electronic transport in  $\text{Li}_2\text{O}_2$ . Nevertheless, the transport mechanism is not yet clear. In a previous paper from our group it was proposed that  $\text{Li}^+$  vacancies create electron holes in the valence band of  $\text{Li}_2\text{O}_2$ , which gives rise to the electronic conduction. However, recent optical absorption experiments have revealed strong excitonic effects in  $\text{Li}_2\text{O}_2$ , which point towards the creation of  $\text{Li}^+$ -Superoxide pairs, instead of holes in the valence band. In this work I will present confirmation of the last hypothesis through DFT+U calculations and propose possible routes for improving  $\text{Li}_2\text{O}_2$  electron conductivity through doping.

O 39.9 Wed 12:30 HE 101

**Signatures of Electronic Correlations in the Narrow Gap Semiconductor FeSi** — ●JAN M. TOMCZAK, KRISTJAN HAULE, and

GABRIEL KOTLIAR — Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA

Correlated semiconductors have been studied intensively over the years, because they exhibit an unusual metallization process which is poorly understood. At low temperatures FeSi behaves as an ordinary semiconductor, while at high temperatures the system is a bad metal with a Curie like susceptibility. Analogies with heavy fermion Kondo insulators and mixed valence compounds, and an anomalous electron-phonon coupling have been invoked to account for this behavior, but lacking quantitative methodologies applied to this problem, a consensus remained elusive to date. Here, we use realistic many-body calculation methods to elucidate the metallization mechanism of FeSi. Our methodology accounts for all substantial anomalies observed in FeSi : lack of conservation of spectral weight in optics, Curie susceptibility and, in particular, an anomalous thermoelectric power. Having quantitatively validated our methodology for this system, we propose a new scenario for FeSi : Unlike in conventional semiconductors the metallization in correlated insulators such as FeSi is induced by the emergence of non-quasiparticle incoherent states in the gap. This temperature induced coherence-incoherence crossover is accompanied by a massive reorganization of the spin excitation spectrum. Besides the fundamental interest, our work is relevant to the design of thermoelectric materials based on correlated insulators.

O 39.10 Wed 12:45 HE 101

**Point defect calculations in  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  using a screened-exchange hybrid functional** — ●JOHAN POHL, ANDREAS KLEIN, and KARSTEN ALBE — Institut für Materialwissenschaft, Petersenstr. 32, D-64287 Darmstadt

We present point defect calculations in  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$  (CIGS) using the screened-exchange hybrid functional HSE06 with adapted screening. The use of a functional that gives a correct band gap is important for this material, which is used as absorber material in solar cells. The resulting formation enthalpies, charge transition levels and migration barriers of native defects are presented and their implications for solar cell performance are discussed. We focus on the properties of the copper vacancy [1], which is responsible for Fermi-level pinning at the buffer-absorber interface in CIGS solar cells, and the copper interstitial [2], whose fast diffusion has been proposed to play a role for the metastable behaviour of CIGS solar cells. The results for other native antisite and vacancy defects are also presented and discussed. Finally, we compare the different pictures of the defect physics of CIGS obtained by the adapted HSE06 functional versus the local generalized gradient functional in order to point out general issues with local functionals for point defect calculations in semiconductors. [1] J. Pohl, K. Albe, *J. Appl. Phys.*, 108, 023509, (2010). [2] J. Pohl, A. Klein, K. Albe, *Phys. Rev. B*, 84, 121201(R), (2011).

O 39.11 Wed 13:00 HE 101

**Entanglement of electron-ion motion and decoherence in trans-polyacetylene oligomers** — ●HEIKO APPEL — {Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Describing decoherence and energy transfer, which is arising after optical excitation in coupled electron-ion systems, is central for the understanding of physical processes appearing in photosynthesis, vision, or in solar-cell applications. As prototypical system for these applications, we investigate in this work the coupled electron-ion dynamics in trans-polyacetylene oligomers which are described by Su-Schrieffer-Heeger Hamiltonians. By tracing the density operator of the combined quantum electron-ion system over either electronic or ionic coordinates, we quantify decoherence, energy transfer and the mutual entanglement in the system after optical excitation.