

CPP 38: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale V (original: O, joined by CPP)

Time: Wednesday 16:00–19:15

Location: TRE Ma

Topical Talk

CPP 38.1 Wed 16:00 TRE Ma
Theory of nonlinear phononics for coherent light-control of solids — ●ANTOINE GEORGES^{1,2,3}, ALASKA SUBEDI², and ANDREA CAVALLERI⁴ — ¹College de France, Paris, France — ²Ecole Polytechnique - CPHT, Palaiseau, France — ³University of Geneva, DPMC, Switzerland — ⁴Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

The use of light to control the structural and electronic properties of solids is an area of great current interest. We present a microscopic theory [arXiv:1311.0544] for ultrafast control of solids with high-intensity Tera-Hertz frequency optical pulses. When resonant with selected infrared-active vibrations, these pulses transiently modify the crystal structure and lead to new collective electronic properties. The theory predicts the dynamical path taken by the crystal lattice using first-principles calculations of the energy surface and classical equations of motion, as well as symmetry considerations. Two classes of dynamics are identified. In the perturbative regime, displacements along the normal mode coordinate of symmetry-preserving Raman-active mode can be achieved by cubic anharmonicities. This validates the mechanism proposed by Först et al. [Nature Physics 7, 854 (2011)] and explains the light-induced insulator-to-metal transition of manganites reported experimentally by Rini et al. [Rini et al. Nature 449, 72 (2007)]. We also predict a new non-perturbative regime in which ultra-fast instabilities that break crystal symmetry can be induced.

CPP 38.2 Wed 16:30 TRE Ma
DFT+Frontier Orbital U — ●EMINE KUCUKBENLI and NICOLA MARZARI — Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne (CH)

Piecewise linearity of the total energy with respect to occupations is not only a fundamental property that should be obeyed by any exact energy functional, but also a starting point to improve approximate functionals that are used in practical applications.

DFT+U enforces piecewise linearity on the Hubbard manifold [1], and it has been shown to greatly improve the accuracy of density-functional theory for transition-metal complexes, thanks to its correction of self-interaction errors [2]. However, it still performs poorly in complexes where significant covalency is present, and intersite corrections (so-called DFT+U+V) have been introduced to improve these challenging cases [3].

Here, we revisit piecewise linearity within the DFT+U and DFT+U+V correction schemes, and explore a novel approach where self-interaction corrections are applied directly to the frontier orbitals. We test this approach on model transition metal complexes, where highly accurate reference results can be established, and on small molecules with varying degrees of covalency.

References: [1] M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 35105 (2005). [2] H. J. Kulik, M. Cococcioni, D. A. Scherlis and N. Marzari, Phys. Rev. Lett. 97, 103001 (2006). [3] V. Leiria Campo Jr and M. Cococcioni, J. Phys. Cond. Matt. 22, 055602 (2010); H. J. Kulik and N. Marzari, J. Chem. Phys. 134, 094103 (2011).

CPP 38.3 Wed 16:45 TRE Ma
Quasiparticle self-consistent GW method with spin-orbit coupling applied to Bi and HgTe — ●CHRISTOPH FRIEDRICH, IRENE AGUILERA, MARKUS BETZINGER, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We present an implementation of the quasiparticle self-consistent (QS) GW method where the spin-orbit coupling (SOC) is fully taken into account in each iteration rather than being added *a posteriori*. The implementation is based on the FLAPW method. The SOC gives rise to spin off-diagonal blocks in the Green function G^{SOC} and the self-energy $\Sigma^{\text{SOC}} = iG^{\text{SOC}}W^{\text{SOC}}$. We applied the QSG^{SOC}W^{SOC} method to the semimetal Bi, which presents in experiment small electron and hole pockets and a tiny band gap (11-15 meV) at the L point, all of them largely overestimated by LDA (e.g., the gap is 86 meV). The QSG^{SOC}W^{SOC} approach predicts a value of the band gap of 8 meV and electron and hole pockets in very good agreement with experiment. The *a posteriori* treatment of the SOC (QSGW+SOC), on the other hand, yields an unphysical result for Bi, predicting it to be a topologi-

cal insulator with a very large gap at L (260 meV) instead of a trivial semimetal. Similarly, for HgTe, QSGW+SOC reorders the bands in a wrong way and opens a gap at the Γ point in disagreement with experiment. In contrast, the QSG^{SOC}W^{SOC} approach yields a qualitatively and quantitatively correct description of the electronic band structure. We acknowledge support from the Helmholtz Association through the Virtual Institute for Topological Insulators (VITI).

CPP 38.4 Wed 17:00 TRE Ma
Studies of semiconducting pyrite and marcasite compounds using many-body perturbation theory in the GW approximation — ●TIMO SCHENA, GUSTAV BIHLMAYER, CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich & JARA, Germany

FeS₂ pyrite and marcasite have recently gained renewed interest as materials for photovoltaic applications, due to their large optical absorption and abundance. Therefore, a reliable description of the fundamental band gap of these compounds within first-principles calculations is desirable. However, common density functional theory (DFT) often suffers from an underestimation of band gaps. This calls for beyond-DFT methods, e.g., the GW approximation, which is known to yield gaps in much better agreement with experiment. Although this is widely accepted for “simple” semiconductors, the situation is not well understood for more complicated cases, where the band edges differ in atomic and orbital character. In fact, we observe an uncommon band gap reduction in FeS₂ when applying single-shot GW on top of DFT, which might be problematic for photovoltaic applications [1]. In this work, we investigate the effects of the GW approximation on a couple of pyrite and marcasite compounds, employing the FLAPW code FLEUR and the GW code SPEX (www.flapw.de). In addition to single-shot GW, we also compare to the results of the recently implemented quasi-particle self-consistent GW approximation. We gratefully acknowledge funding from BMBF of the NADNum project 03SF0402A.

[1] T. Schena *et al.* Physical Review B (accepted 2013)

15 min. break

CPP 38.5 Wed 17:30 TRE Ma
Probing d-band Quantum Well States in Palladium Nanofilms — ●SRIJAN KUMAR SAHA¹, SUJIT MANNA¹, MAREK PRZYBYLSKI^{1,2}, VALERI STEPANYUK¹, and JURGEN KIRSCHNER^{1,3} — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — ²Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, 30-059 Kraków, Poland — ³Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

We present the results of our new study which probes the d-bands quantum well (QW) states in Pd nanofilms grown on Cu(001) using first-principles density functional theory (DFT) calculations combined with scanning tunneling spectroscopy (STS) experiments. This study reveals that QW states occur in the overlayer films of Pd over a strikingly large film thickness (up to 17 monolayers) and in a large binding energy range (from 0.1 to 3.0 eV below Fermi level), thanks to its distinct and broad 4d-bands. The orbital characters of these states are unambiguously identified by our DFT calculations. Calculations also demonstrate oscillatory multilayer relaxations and d-derived quantum size oscillations in Pd films. The pseudomorphic growth, well-defined interface, and spatially resolved STS allows us to probe individual occupied QW states and extract the accurate dispersion of the (Δ_5 -like) d electronic band, as these states are laterally highly localized and give rise to distinct and sharp feature in the tunneling spectra.

CPP 38.6 Wed 17:45 TRE Ma
Implementation and analysis of a plane wave and real space pseudopotential method including an efficient spin-orbit coupling treatment tailored to calculate the electronic structure of large-scale semiconductor nanostructures — ●FRANK ZIRKELBACH, PIERRE-YVES PRODHOMME, JEROME JACKSON, and GABRIEL BESTER — Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

The implementation of the *large-scale atomic effective pseudopoten-*

tial program to solve the Schrödinger equation of an electronic system is discussed. *Atomic effective pseudopotentials* that are derived from screened local effective crystal potentials of self-consistent density functional theory (DFT) calculations are utilized, which ensure an accurate treatment at reduced computational costs. The capability of describing relevant electronic eigenstates of a quantum dot structure consisting of hundred thousand atoms at an atomistic *ab initio* level comparable to DFT is demonstrated. The possibility to represent the wavefunction and to evaluate parts of the Hamiltonian either in a plane wave or real space basis allows for a coherent analysis of various different approaches. In the fully real space treatment, linear scaling with respect to the system size is achieved. The convergence behavior of the different methods and utilized approximations is shown. Furthermore, an efficient spin-orbit treatment different to previously existing implementations within the pseudopotential formalism is outlined. The accuracy of the method is demonstrated via direct comparison to standard DFT codes.

CPP 38.7 Wed 18:00 TRE Ma

Strong Parallelization of Real-Space DFT Calculations — ●ANDREA NOBILE^{1,2}, PAUL BAUMEISTER^{1,2}, DANIEL WORTMANN¹, and STEFAN BLÜGEL¹ — ¹Peter Grünberg Institut & Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — ²Jülich Supercomputing Center, Forschungszentrum Jülich, 52425 Jülich, Germany

The rapid change in modern supercomputing architectures poses a challenge to well established DFT codes. In particular, the increase in raw floating point power obtained through parallelism at different levels is not easily exploitable by using the traditional direct diagonalization methods. We will present our new real-space Projector Augmented Wave (PAW) implementation. The real-space representation of the wave functions, densities and potentials, enables the usage of very flexible boundary conditions and naturally adapts to massively parallel architectures. Parallelism can be exploited in the form of domain decomposition of the three dimensional grid, k-point sampling and bands. The kinetic energy operator, realized as a finite difference stencil, is localized. As a consequence the real-space representation of the Hamiltonian is sparse. This limits the amount of necessary communications and allows an application of the operator to a trial vector in order(N) operations. We will present results about the efficiency of the most numerical intensive parts of the code and we will compare the accuracy of the calculations for reference systems with other established DFT methods.

CPP 38.8 Wed 18:15 TRE Ma

Rare Earth Metals in Density-Functional Theory — ●MARCO CASADEI¹, XINGUO REN², PATRICK RINKE¹, ANGEL RUBIO^{1,3}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of Technology, Hefei, China — ³NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

The presence of *f* electrons in the rare earths and their interaction with the *s* and *p* electrons give rise to several physical phenomena. One prominent example is the isostructural α - γ phase transition in cerium (Ce). We have shown that density-functional theory (DFT) captures the volume collapse associated with the transition, but only if advanced functionals such as exact exchange plus correlation in the random-phase approximation (EX+cRPA) are used [1]. The volume collapse is understood in terms of a *localization/delocalization* of the *f* electrons. We then addressed the question: *is the isostructural volume collapse in cerium unique?* By applying DFT, we studied lanthanum (La), praseodymium (Pr) and neodymium (Nd), which undergo several structural changes with pressure. We find that the transitions are already captured at a lower level of DFT (i.e. with (semi)-local functionals) and therefore conclude that *f*-electrons are not the driving force in this case. Within hybrid functionals, we find only one phase in lanthanum, which has no *f*-electrons, and more than one stable solution in the fcc crystal for Pr and Nd, as found for Ce. Unlike in Ce, however, there is always one solution that is the most stable, thus no isostructural volume collapse emerges in agreement with experiments. [1] M. Casadei *et al.*, Phys. Rev. Lett. **109**, 14642 (2012).

CPP 38.9 Wed 18:30 TRE Ma

Electronic Structure and van der Waals Interactions in the Stability and Mobility of Point Defects in Semiconductors — ●WANG GAO and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der MPG, Berlin, Germany

Point defects are abundant in materials, and significantly affect the electronic, optical, and magnetic properties of solids. However, our understanding of the stability and mobility of point defects remains incomplete, despite decades of intensive work on the subject. In the framework of density-functional theory, Perdew-Burke-Ernzerhof functional underestimates formation energies by 0.7 eV due to the electron self-interaction error, while Heyd-Scuseria-Ernzerhof (HSE) functional yields formation energies in better agreement with high-level many-body methods, but often overestimates migration barriers by up to 0.4 eV.

Using HSE coupled with screened long-range vdW interactions [1], we demonstrate that HSE+vdW can simultaneously and accurately describe the formation energies and migration barriers of point defects. The inclusion of vdW interactions significantly changes the transition state geometries, and brings migration barrier into close agreement with experimental values for six different defects. For multiatom vacancies and point defects in heavier semiconductors, vdW interactions play an increasingly larger role [2].

[1] G. X. Zhang, *et al.*, PRL **107**, 245501 (2011); A. Tkatchenko, *et al.*, PRL **108**, 236402 (2012).

[2] W. Gao and A. Tkatchenko, PRL **111**, 045501 (2013).

CPP 38.10 Wed 18:45 TRE Ma

Scaling Laws for van der Waals Interactions in Nanostructured Materials — ●VIVEKANAND GOBRE and ALEXANDRE TKATCHENKO — Fritz Haber Institut der MPG, Berlin

Accurate description of van der Waals (vdW) interactions is crucial for precise prediction of structure and stability of complex materials. VdW forces originate from interactions between fluctuating multipoles in matter and play a significant role in the self-assembly of nanostructured materials. Many models used to describe vdW interactions in nanomaterials are based on a simple pairwise-additive approximation, neglecting the strong electrodynamic response effects caused by long-range fluctuations in matter. We develop and utilize an efficient microscopic method [1,2] to demonstrate that vdW interactions in nanomaterials act at distances greater than typically assumed, and can be characterized by different scaling laws depending on the dimensionality and size of the system. Specifically, we study the behaviour of vdW interactions in single-layer and multilayer graphene, fullerenes of varying size, single-wall carbon nanotubes and graphene nanoribbons. As a function of nanostructure size, the van der Waals coefficients follow unusual trends for all of the considered systems, and deviate significantly from the conventionally employed pairwise-additive picture. We propose that the peculiar van der Waals interactions in nanostructured materials could be exploited to control their self-assembly. [1] Tkatchenko, DiStasio, Car, and Scheffler, PRL (2012); [2] Gobre, Tkatchenko, Nat. Commun. (2013).

CPP 38.11 Wed 19:00 TRE Ma

2D nanopatterns of shape-persistent molecular polygons on HOPG — ●STEFAN-S. JESTER, NINA SCHÖNFELDER, EVA SIGMUND, and SIGURD HÖGER — Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Shape-persistent organic molecules with flexible side chains self-assemble at the solution/solid interface to form 2D nanoarchitectures. Scanning tunneling microscopy yields a submolecularly resolved insight into the adsorbate structures. A key issue is how the shape and symmetry of the backbones and their alkyl chain substitution pattern determine the shape and symmetry of the adsorbate patterns. Recently we focused on molecular polygons (triangles, squares, pentagons, and hexagons) with dithiophene corners and phenylene-alkynylene sides.[1] In my talk I will give insight into the relation between Archimedean surface patterns and supramolecular 2D adlayers. [1] S.-S. Jester, E. Sigmund, S. Höger *J. Am. Chem. Soc.* **2011**, *133*, 11062.