

O 7: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale

Non-equilibrium processes such as charge and heat transport are central to electronic and thermoelectric applications. Understanding these phenomena at the nanoscale challenges both theory and experiment. Basic theoretical issues are related to the role of quantum mechanics, the interplay of ballistic, diffusion and hopping processes, the importance of dissipation, the effect of electronic correlation, and the signatures of unusual quantum states. On the experimental side devising measurements to unravel these phenomena in a controlled way poses severe difficulties. In this regard, optical lattices of cold atoms are emerging as a powerful laboratory to test theoretical models and discover unforeseen phenomena.

This symposium will cover current issues in the field by bringing together scientists working in different specific areas with the aim of fostering interdisciplinary discussion, assessing current theoretical understanding, and indicating future goals with emphasis on electronic structure theory.

Organizers: Roberto Car (Princeton), Kristian S. Thygesen (Lyngby) and Matthias Scheffler (Berlin)

Time: Monday 10:30–13:15

Location: TRE Ma

Topical Talk

O 7.1 (74) Mon 10:30 TRE Ma

Molecular junction transport: some theoretical and computational considerations — ●MARK RATNER¹ and MATTHEW REUTER² — ¹Chemistry, Northwestern University, Evanston Illinois 60208 USA — ²Chemistry, Northwestern University, Evanston Illinois 60208 USA

Following the development of break junction techniques, and very elegant measurements by many labs worldwide, the understanding of the community for single molecule transport junctions on the experimental side has been very nicely unified. While there are still challenges, interpretations of the transport (and indeed of some second-order response properties) is now quite sophisticated.

There have been major advances in the computational approaches also, and in many cases, computations and measurements can be compared quantitatively. But there are some remaining difficulties in the computational and theoretical approaches, and this talk will discuss a few of them.

The topics addressed will be: single molecule aspects, histograms and their usage, time-dependence of the transport, and ghost transmission and computational accuracy.

O 7.2 (442) Mon 11:00 TRE Ma

On the description of biased nanocontacts from ab initio — ●STEVEN ACHILLES¹, JÜRGEN HENK¹, MICHAEL CZERNER², CHRISTIAN HELLIGER², and INGRID MERTIG¹ — ¹Institute of Physics, Martin Luther University Halle-Wittenberg, D-06099 Halle, Germany — ²I. Physikalisches Institut, Justus Liebig University, D-35392 Giessen, Germany

A suitable description of arbitrary shaped and biased nanocontacts is very important for investigating and predicting physical effects of materials on the nanometer scale. In particular, the electronic transport properties under finite bias voltages are of great interest.

To account for systems under finite bias we extended our Korrington-Kohn-Rostoker Green's function method [1] to the Keldysh formalism [2]. The method was developed for different types of geometries, i.e. planar junctions [3] and embedded real-space clusters [4]. Both implementations include a self-consistent treatment of the electronic structure under external bias using the nonequilibrium density.

We present ab initio results of voltage drops, the charge relaxation under finite bias voltage and current-voltage characteristics for different types of geometries.

[1] R. Zeller, P.H. Dederichs, B. Ujfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B 52, 8807 (1995); P. Zahn, I. Mertig, R. Zeller, and P.H. Dederichs, Mat. Res. Soc. Symp. Proc. 475, 525 (1997).

[2] L.V. Keldysh, Sov. Phys. JETP 20 (4), 1018-1026 (1965).

[3] S. Achilles et al., Phys. Rev. B 88 (12), 125411 (2013).

[4] S. Achilles et al., to be published

O 7.3 (772) Mon 11:15 TRE Ma

Elasticity changes in molecular junctions under bias: an ab-initio study — ●CLOTILDE S. CUCINOTTA¹, MELIN BAI^{1,2}, IVAN RUNGGER¹, SHMIN HOU², and STEFANO SANVITO¹ — ¹School of Physics and CRANN, Trinity College Dublin, College Green, Dublin 2, Ireland — ²Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, China

Non-conservative current induced forces are at the origin of a rich variety of dynamical processes, including vibrations, rotations, phonon energy flow, desorption and reactions. The ability to simulate these phenomena paves the way for crucial advances in interface physics and in molecular electronics. New insights into how the presence of non-conservative forces can affect the vibrational spectrum of prototypic Au-H₂-Au nano-junctions are obtained by the Non Equilibrium Green Functions approach combined with Density Functional Theory as implemented in the Smeagol code [1]. The modification of the phonon spectrum of the junction in the presence of an external bias is for the first time analysed, in terms of charge redistribution caused by the electron flow, potential drop and differences in an average distance collective variable. Phonon modes changes are related to a change in bias of some of the elastic constants. The importance of electric field vs. current effects is compared. The elasticity changes of the molecular junction with bias are interpreted in terms of the current flowing through the system. [1] <http://www.smeagol.tcd.ie/SmeagolDownloads.htm>.

O 7.4 (315) Mon 11:30 TRE Ma

Carbon nanotubes decorated with magnetic clusters: magnetism, electron transport and gas sensing — ●ZEILA ZANOLLI¹ and JEAN-CHRISTOPHE CHARLIER² — ¹Forschungszentrum Juelich, PGI and IAS, Juelich, Germany — ²IMCN, Université catholique de Louvain (UCL), Belgium

In this work, first-principles techniques and non-equilibrium Green's function approaches are used to investigate magnetism and spin-polarized quantum transport in carbon nanotubes (CNTs) decorated with transition metal magnetic nanoclusters (NC).

For small cluster sizes (< 1 nm), *ab initio* calculations predict a considerable local magnetic moment that induces spin polarization in the host CNT due to a strong mutual interaction with the magnetic NC. Such a huge local magnetic perturbation can be tailored by molecular adsorption on the metallic NC, thus modifying both the magnetization and the spin-dependent conductance of the hybrid CNT-NC system. The adsorption of benzene on Ni- or Pt-decorated metallic CNTs has been investigated as a test case. The *ab initio* simulations demonstrate that the magnetization change due to the absorption of a single C₆H₆ molecule should be large enough to be detected experimentally using either magnetic-AFM or SQUID magnetometer. Consequently, the present research suggests a novel approach for single molecule gas detection, based on local magnetic moment measurements in CNT-NC hybrid systems [1].

[1] Z. Zanolli, J.-C. Charlier, ACSnano 6 (2012) 10786-10791.

15 min. break

Topical Talk

O 7.5 (37) Mon 12:00 TRE Ma

Insight into Charge Transport in Molecular Junctions from Ab Initio Theories of Level Alignment — ●JEFFREY B. NEATON — Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, USA — Department of Physics, University of California, Berkeley, Berkeley, CA — Kavli Energy Nanosciences Institute, Berkeley, CA

Recent scanning tunneling microscope-based break-junction experiments of molecular junctions – devices formed by trapping organic molecules between macroscopic metallic electrodes – have reported robust conductance, thermopower, switching behavior, quantum in-

terference effects, spin-filtering phenomena, and even nonlinear effects such as rectification, establishing such junctions as unique and revealing windows into the physics of charge transport at the molecular scale. In this talk, I will summarize a predictive approach to compute and understand the transport properties of molecular junctions with good accuracy. Our approach includes important exchange and correlation effects missing in standard DFT Kohn-Sham junction level alignment, building on self-energy corrections within a GW approximation. Advantages and limitations of our approach will be discussed quantitatively in the context of a direct comparison with recent photoemission and transport measurements. I will also describe applications of this approach to select junctions exhibiting novel trends in conductance, thermopower, and nonlinear IV characteristics, where new physical insight is obtained by relating computed transport phenomena to junction structure and chemistry.

O 7.6 (135) Mon 12:30 TRE Ma

Towards First-Principles Modeling of Solvent Effects in Photo-Catalytic Water Splitting — ●STEFAN RINGE, HARALD OBERHOFER, SEBASTIAN MATERA, and KARSTEN REUTER — Technische Universität München, Germany

In the context of solar energy conversion the search for new materials for photo-catalytic water splitting has received new impetus. While in general powerful, computational screening approaches are struggling with the complexity of the underlying physical processes at the solid-liquid interface. Recent work points in particular at the necessity to include at least an efficient description of solvent screening effects to compute meaningful descriptors even in simple computational hydrogen electrode approaches. To this end, we present an implementation of the modified Poisson-Boltzmann (MPB) implicit solvation model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. Optimally integrating into this code environment, we solve the MPB equation in a novel approach based on an expansion of the electrostatic potential in the localized basis functions of FHI-aims. In contrast to common numerical multi-grid solvers this approach can directly make use of the optimized integration schemes used to reach self-consistency and removes the need for numerical interpolation between different grids. We demonstrate the approach and its efficiency for a range of molecular test systems, and show first results for catalytic water splitting on gold nano-clusters.

O 7.7 (249) Mon 12:45 TRE Ma

Towards a combined QM/MM and implicit solvent descrip-

tion of photoelectrochemical processes — ●MARKUS SINSTEIN¹, DANIEL BERGER¹, RAN JIA², VOLKER BLUM³, HARALD OBERHOFER¹, and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²Jilin University, P.R. China — ³Duke University, USA

Photoelectrochemical systems are widely explored to drive energy-relevant redox reactions like water splitting or CO₂ reduction. The detailed analysis of the involved elementary processes via first-principles calculations is challenged by the necessity to simultaneously account for the extended semiconductor photocatalyst and the liquid electrolyte. Especially for charge (proton and/or electron) transfer steps traditionally employed periodic boundary condition approaches involve charged supercells with difficult to control finite size errors. To this end, we present a solid state QM/MM embedding approach, in which only a finite cluster model of the photocatalyst surface is treated quantum mechanically and the correct Madelung potential of the periodic system is obtained by embedding into a charge field. For the efficient modeling of photoelectrochemical processes we combine this approach with an implicit solvation scheme within the DFT package FHI-aims. Finally, we also show early test results of the combined QM/MM implicit solvent model.

O 7.8 (414) Mon 13:00 TRE Ma

Ab-initio Simulation of Molecular Networks on the Surface of Water — ●RALPH KOITZ, MARCELLA IANNUZZI, ARI P SEITSONEN, and JÜRIG HUTTER — University of Zurich, Zurich, Switzerland

Molecules adsorbed on surfaces play an important role in catalysis, surface science, and nanotechnology. Traditionally, research has focused on various adsorbates atop metals and metal oxides using computational and surface-science techniques. More recently, however, it was demonstrated that ordered monolayer networks can also be formed on the surface of liquid water by using metal ions to bind together multidentate precursor molecules. As these assemblies are difficult to characterize, computational methods can provide valuable insight into their formation and structure.

In this contribution we present large-scale DFT-based molecular dynamics simulations of the formation of a network of *tris*-terpyridine-derived molecules (TTPB) on a water slab. In particular, we focus on the structure of the molecule on the surface, the mechanism of Zn²⁺ ion insertion from the solution and the subsequent linking of molecules into aggregates. We employ the metadynamics method to quantify the free energy surface of the involved processes. Our results provide detailed insight into on-surface and subsurface diffusion in this system and chemical reactions of TTPB on the surface of water.

O 15: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale II

Time: Monday 16:00–18:45

Location: TRE Ma

Topical Talk O 15.1 (72) Mon 16:00 TRE Ma
Simulating heat transport: from large scale molecular dynamics to first-principles calculations — ●DAVIDE DONADIO — Max Planck Institute for Polymer Research, Mainz, Germany

The necessity to design materials and devices able to harness thermal energy, and possibly convert it into more amenable energy forms, has stimulated a major effort in the scientific community to understand heat transport at the mesoscale and the nanoscale. In this talk I will discuss different atomistic approaches to simulate nanoscale heat transport, ranging from large scale molecular dynamics simulations with classical empirical potentials at equilibrium and non-equilibrium conditions, to lattice dynamics calculations with force-constants computed by first principles. Applications will include silicon and carbon nanostructures, phase-change materials and molecular junctions.

O 15.2 (173) Mon 16:30 TRE Ma
First principles study of thermal conductivity cross-over in nano-structured Zinc-Chalcogenides — ●ANKITA KATRE¹, ATSUSHI TOGO², RALF DRAUTZ¹, and GEORG K. H. MADSEN¹ — ¹ICAMS, Ruhr-Universität Bochum, 44801 Bochum, Germany — ²ESISM, Kyoto University, Sakyo, Kyoto 606-8501, Japan

Nano-structured Zinc-Chalcogenides are interesting for thermoelectric applications due to their low thermal conductivity.[1] A simple model study has reported how the thermal conductivity of ZnS, ZnSe and ZnTe can potentially show a cross-over as a function of the maximal mean free path of the phonons.[2] We have applied the Boltzmann transport equation in the relaxation time approximation to verify this. We find that thermal conductivity of ZnS crosses ZnSe and ZnTe and explain this in terms of the different contributions of phonon modes in these materials. Furthermore, the cross-over is found to be strongly influenced by isotope scattering. The calculated thermal conductivity is found to be strongly dependent on the volume and we explain the observed differences between LDA and GGA calculations. We compare further calculated thermal properties, such as the thermal expansion coefficient, to experiment to validate our approach.

[1] L.Zhen, S.Qiao, D.Y.Xiang, H.Z.Zhong, and Q.L.Gao, *J. Mater. Chem.* **22**, 22821 (2012). [2] N.Mingo and D.Broido, *Phys. Rev. Lett.* **93**, 246106 (2004).

O 15.3 (203) Mon 16:45 TRE Ma
Density-functional perturbation theory for lattice dynamics with numeric atom-centered orbitals — ●HONGHUI SHANG, CHRISTIAN CARBOGNO, PATRICK RINKE, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin

The response of the electronic structure to atomic displacements gives rise to a variety of interesting physical phenomena, which can be probed by experimental techniques such as infrared or Raman spectroscopy or neutron diffraction. The response can be conveniently computed from first principles by means of density-functional perturbation theory (DFPT). Here we present our implementation in the all-electron atom-centered numeric orbital code FHI-aims [1]. Our approach combines the accuracy of an all-electron full-potential treatment with the computational efficiency of localised atom-centered basis sets that is necessary to study large and complex systems. We verified the accuracy of our DFPT implementation by comparing the vibrational frequencies to finite-difference reference calculations and literature values. Due to the atom-centered nature of the integration grids in FHI-aims, the portion of the grid that belongs to a certain atom also moves when this atom is displaced. Here we demonstrate that, unlike for first derivatives (i.e. forces) [2], this moving-grid-effect plays an important role for second derivatives (i.e. vibrational frequencies). Further analysis reveals that predominantly diagonal force constant terms are affected, which can be bypassed efficiently by invoking translational symmetry.

[1] V. Blum et al. *Comp. Phys. Comm.* **180**, 2175 (2009)

[2] B. Delley, *J. Chem. Phys.* **94**, 7245 (1991).

O 15.4 (385) Mon 17:00 TRE Ma
Breakdown of Fourier law in layered materials — ●ANDREA CEPPELOTTI¹, GIORGIA FUGALLO², FRANCESCO MAURI³, and NICOLA MARZARI¹ — ¹THEOS, École Polytechnique Fédérale, Lausanne —

²IMPIC, Université Pierre et Marie Curie, Paris — ³LSI, École Polytechnique, Paris

We compute the thermal conductivity in crystalline layered materials by solving the Boltzmann Transport Equation (BTE) for phonons [1], with the phonon-phonon collision rates obtained from density-functional perturbation theory. We find that in 2D materials, such as graphene and related compounds, and even in 3D layered materials, like bulk graphite, the single-mode relaxation time approximation (SMRTA) cannot describe heat transport correctly, underestimating by one order of magnitude or more thermal conductivities and phonons' mean free paths. Instead, we show that the exact self-consistent solution of the BTE provides results in excellent agreement with experimental measurements [2]. The shortcomings of the SMRTA lie in the assumption that heat flow is transferred only by individual phonon excitations, whereas in layered materials the transport can only be explained in terms of collective phonon excitations. The characteristic length of these collective excitations is often comparable with that of the experimental sample - as a result, Fourier's law become questionable, since its statistical nature makes it applicable only to systems larger than a few mean free paths.

[1] G. Fugallo et al., *Phys. Rev. B*, **88**, 045430 (2013).

[2] A. A. Balandin, *Nat. Mater.* **10**, 569 (2011).

O 15.5 (653) Mon 17:15 TRE Ma
High Temperature Thermal Conductivity from First Principles — ●CHRISTIAN CARBOGNO¹, RAMPI RAMPRASAD², and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Chemical, Materials & Biomolecular Engineering, University of Connecticut, Storrs, USA

In spite of significant research efforts, a first principles determination of the thermal conductivity at high temperatures has remained elusive. Under such conditions, Boltzmann transport techniques [1] that include anharmonic effects only perturbatively become inaccurate or even inapplicable. In this work, we overcome this limitation by performing first-principles Green-Kubo simulations [2], in which all orders of anharmonicity are incorporated by the means of *ab initio* molecular dynamics. The thermal conductivity is then assessed from the auto-correlation function of the heat flux in thermodynamic equilibrium. We discuss the details of our implementation and the definition of our heat flux that is based on the virial theorem. We validate our approach by presenting calculations for ZrO₂ that also showcase the importance of higher order anharmonic effects in materials with low thermal conductivities. Eventually, we discuss how our technique can be coupled to multi-scale models to achieve a computationally efficient and accurate description of the thermal conductivity at the nanoscale.

[1] D. A. Broido et al., *Appl. Phys. Lett.* **91**, 231922 (2007).

[2] R. Kubo, M. Yokota, S. Nakajima, *J. Phys. Soc. Jpn.* **12**, 1203 (1957).

O 15.6 (283) Mon 17:30 TRE Ma
Accurate Modelling of the Polymorphism and Elastic Response of Molecular Materials from First Principles — ●ANTHONY REILLY and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der MPG, Berlin, Germany

Molecular materials are of great fundamental and applied importance in science and industry, with numerous applications in pharmaceuticals, electronics, sensing, and catalysis. A key challenge for theory has been the prediction of their stability, polymorphism and response to perturbations. While pairwise models of van der Waals (vdW) interactions have improved the ability of density functional theory (DFT) to model these systems, quantitative and even qualitative failures often remain. Here, we show how a many-body description of vdW interactions can dramatically improve the accuracy of DFT for molecular materials, yielding quantitative description of stabilities and polymorphism for these challenging systems. Moreover, the role of many-body vdW interactions goes beyond stabilities to response properties. In particular, we have studied the elastic properties of a series of molecular crystals, finding that many-body vdW interactions can account for up to 30% of the elastic response, leading to quantitative and qualitative changes in elastic behavior. We will illustrate these crucial effects with the challenging case of the polymorphs of aspirin, leading to a

better understanding of the conflicting experimental and theoretical studies of this system.

O 15.7 (104) Mon 17:45 TRE Ma

Surface chemistry on nanostructured oxides: do we have to go beyond hybrid DFT? — •DANIEL BERGER, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München, Germany

Nanostructured oxide surfaces are promising candidates for a wide range of energy and catalysis applications. For first-principles modeling of corresponding surface chemical reactions the current state-of-the-art is generally defined by hybrid-level density-functional theory (DFT). Systematic work assessing the achieved accuracy at this level is nevertheless scarce, also owing to the fact that higher-level reference methods are often not available for standard periodic boundary condition supercell calculations. To this end, we present a study benchmarking semi-local and hybrid DFT against (renormalized) second-order perturbation theory (MP2,rPT2) as recently implemented in the FHI-aims package [1]. We make the efficient usage of the latter theories for oxide surfaces possible through a solid-state embedding framework, in which a central cluster region is described quantum mechanically, the long-range electrostatic interactions in the oxide are accounted for through a polarizable monopole field, and a shell of norm-conserving pseudopotentials correctly connects the two regions. We illustrate the performance of the various levels of theories using the water-splitting reaction at ideal and defected TiO₂(110) surfaces as showcase. [1] X. Ren *et al.*, Phys. Rev. B **88**, 035120 (2013)

O 15.8 (668) Mon 18:00 TRE Ma

Atoms-in-solids perspective on polarizabilities and van der Waals coefficients in semiconductors — •GUO-XU ZHANG, ANTHONY M. REILLY, ALEXANDRE TKATCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin, Germany

The calculation of response properties of solids including their polarizabilities and van der Waals (vdW) coefficients usually requires the knowledge of the full electronic bandstructure. For non-covalently bound solids, such as noble-gas and ionic crystals, atoms-in-solids model can be successfully utilized to define their polarizabilities. Here we critically assess the atoms-in-solids model for covalently-bound solids, ranging from wide-gap (10 eV) to narrow-gap (below 1 eV) semiconductors. We model their response by assigning a single quantum harmonic oscillator to every atom, where the parameters of the oscillators are defined as functionals of the electron density, following the Tkatchenko-Scheffler method [1]. The response function is then calculated by solving self-consistent screening equations of classical electrodynamics, without any explicit information about the electronic bandstructure [2]. The calculated polarizabilities and vdW coefficients for 23 semiconductors are compared with TDDFT and experimental benchmark data, revealing an overall agreement within 10%. The efficiency of our method and the accuracy of the calculated vdW parameters allows us to demonstrate the crucial role of vdW interactions in the cohesive properties of the 23 semiconductors. [1] Tkatchenko and Scheffler, PRL (2009); [2] Tkatchenko, DiStasio, Car, Scheffler, PRL (2012).

O 15.9 (839) Mon 18:15 TRE Ma

Adsorption at semiconductor surfaces - an energy analysis method — •RALF TONNER and MARC RAUPACH — Fachbereich Chemie & Materials Sciences Centre, Philipps-Universität Marburg, Germany

The chemical bond is one of the most fundamental concepts in chemistry. Classifications such as covalent, ionic or metallic bonding are central in discussing trends in different compounds and predicting new reactivity. Several very helpful concepts and methods were developed to understand the chemical bond at surfaces.[1] The question about energetic contributions to surface chemical bonds on the other hand did not receive great attention although energy changes are the ultimate driving force in bond formation.

Starting from preliminary work by Philippsen and Baerends,[2] we implemented all terms of an Energy Decomposition Analysis (EDA) to obtain quantitative data about energetic contributions to chemical bonding in periodic systems. This periodic EDA method was applied to questions of chemisorption of organic molecules at semiconductor surfaces where it can shed light on the nature of the surface-adsorbate bonds.

[1] a) A. Nilsson, L. G. M. Pettersson, J. Nørskov, Chemical Bonding at Surfaces and Interfaces, Elsevier, Amsterdam, 2007; b) A. Groß, Theoretical Surface Science, Springer, Berlin, Heidelberg, 2009. [2] P. H. T. Philippsen, E. J. Baerends J. Phys. Chem. B 2006, 110, 12470.

O 15.10 (311) Mon 18:30 TRE Ma

Non-local density functionals meet many-body dispersion: A hybrid approach for van der Waals interactions — •JAN HERMANN, MATTHIAS SCHEFFLER, and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Different approaches to treating van der Waals (vdW) interactions in density-functional theory can be loosely divided into the atom-based and the ones based on non-local functionals. The first type comprises a range of methods from atom-pairwise additive schemes by Grimme to many-body dispersion (MBD) approach of Tkatchenko et al. Usually, these methods require precalculated atomic parameters and thus rely on information not explicitly contained in the electron density. The other category consists of nonlocal functionals either of the Langreth and Lundquist or the Vydrov and van Voorhis (VV) type. In these approaches, the vdW interaction is obtained as a functional of the electron density and at most a few tuning parameters are needed.

Here, we show that these two contrasting approaches can be synergistically combined. We use the polarizability from the nonlocal functional of VV within the MBD method of Tkatchenko et al. Such a combination is worthy for several reasons. First, it is an atom-centered approach with no atomic parameters. Second, it puts aside the problem of partitioning electron density between atoms, which can be problematic in some cases. Third, it enables more direct comparison of so far unrelated methods. Fourth, it highlights the idea of combining working elements from different approaches.

O 28: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale III

Time: Tuesday 10:30–13:15

Location: TRE Ma

Topical Talk O 28.1 (71) Tue 10:30 TRE Ma
Ultrafast relaxation dynamics of Hubbard nanoclusters —
 ●MICHAEL BONITZ¹, SEBASTIAN HERMANN¹, CHRISTOPHER HINZ¹, and DENIS LACROIX² — ¹Institut für Theoretische Physik und Astrophysik, CAU Kiel, Leibnizstr. 15, 24098 Kiel — ²IPN Orsay, 15 Rue Georges Clemenceau, 91406 Orsay

With the growing availability of intense short-pulse radiation sources it becomes possible to drive interacting many-particle or few-particle systems out of equilibrium in a controlled way. The subsequent relaxation and equilibration dynamics is still poorly understood. From a theory point of view these processes are complicated due to the simultaneous dynamics of the occupation functions and of binary correlations. The problem becomes even more complicated when the system has finite size and is spatially inhomogeneous [1]. The Hubbard model is a prototype for treating correlation effects in condensed matter or molecular systems fully including finite size and inhomogeneity effects. We, therefore, concentrate on the relaxation dynamics of small 1D, 2D and 3D Hubbard clusters that contain from a few to several hundred electrons. We observe a complex multi-stage relaxation behavior that depends on the external excitation, on the coupling strength and on the geometry of the system. In this talk we present results from two complementary theoretical approaches: first, from nonequilibrium Green functions where we apply the Generalized Kadanoff Baym ansatz [1] and, second, from a stochastic mean field approach.

[1] K. Balzer, and M. Bonitz, “Nonequilibrium Green’s Functions Approach to Inhomogeneous Systems”, Lect. Notes Phys. **867** (2013)

O 28.2 (260) Tue 11:00 TRE Ma
Exact adiabatic approximation in TDDFT — ●JEIRAN JOKAR and NICOLE HELBIG — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The use of functionals from static density functional theory in an adiabatic way in a time-dependent framework is known to cause various problems due to the resulting exchange-correlation kernel being frequency independent. In order to isolate the effects which are due to the adiabatic approximation we calculate the exact static potential for two electron systems. Before using this potential in an adiabatic way in a time propagation we need to ensure that the potential is well defined also at those parts of space where the density is small as they might become more populated at a later time. We use the exact adiabatic approximation to describe Rabi oscillations, i.e. the oscillation between the ground state and an excited state when a monochromatic laser with a frequency close to the resonance is applied.

O 28.3 (619) Tue 11:15 TRE Ma
Real-time propagation of coupled Maxwell-Schrödinger and time-dependent Kohn-Sham-Maxwell systems — ●RENÉ JESTÄDT¹, HEIKO APPEL¹, and ANGEL RUBIO^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²NanoBio Spectroscopy group and ETSEF, Universidad del País Vasco, San Sebastián, Spain

Based on the Riemann-Silberstein vector of the electromagnetic field, we formulate Maxwell’s equations in a symplectic spinor representation similar to the Dirac equation. This spinor representation allows us to use standard unitary propagation techniques developed for the Schrödinger equation [1] also for Maxwell’s equations and simplifies a coupled solution of Maxwell’s and Schrödinger’s equations. To illustrate our approach, we present the real-time evolution of atomic systems embedded in optical waveguides and dielectric nanostructures. The coupling of Maxwell’s equations to the time-dependent Kohn-Sham equations is a basic ingredient for the development of a time-dependent density functional theory formulation of quantum electrodynamics [2]. As an extension of our work on coupled Maxwell-Schrödinger systems, we show first steps of an implementation of Maxwell’s equations coupled to the time-dependent Kohn-Sham equations in the first principles real-space real-time code octopus [3].

[1] A. Castro et al., J. Chem. Phys. **121** (2004).

[2] M. Ruggenthaler, F. Mackenroth, and D. Bauer, Phys. Rev. A **84**, 042107 (2011); I. Tolkatly, Phys. Rev. Lett. **110**, 233001 (2013).

[3] X. Andrade et al., J. Phys. Cond. Mat. **24** (2012).

O 28.4 (616) Tue 11:30 TRE Ma
Nonlinear optics by means of the dynamical Berry phase: Application to second- and third-harmonic generation — ●CLAUDIO ATTACALITE¹ and MYRTA GRUNING² — ¹Univ. Grenoble Alpes/CNRS, Institut Neel, F-38042 Grenoble, France — ²School of Mathematics and Physics, Queen’s University Belfast, Belfast BT7 1NN, Northern Ireland, UK

We present a real-time approach to study nonlinear optical properties in Condensed Matter systems that is especially suitable for crystalline solids. The equation of motions and the coupling of the electrons with the external electric field are derived from the Berry phase formulation of the dynamical polarization. Many-body effects are introduced by adding single-particle operators to the independent-particle Hamiltonian. Specifically we include crystal local field effects, renormalization of the energy levels and excitonic effects. The approach is validated by calculating the second and third harmonic generation of bulk semiconductors. Finally we present second-harmonic generation spectrum of h-BN or MoS2 monolayers and show that correlation effects double the signal intensity at the excitonic resonances with respect to the contribution from independent electronic transitions.

References: [1] Nonlinear optics from ab-initio by means of the dynamical Berry-phase <http://arxiv.org/abs/1309.4012> [2] Second Harmonic Generation in h-BN and MoS2 monolayers: the role of electron-hole interaction <http://arxiv.org/abs/1310.7459>

15 min. break

O 28.5 (372) Tue 12:00 TRE Ma
Accurate Correlation Energies from Adiabatic Time-Dependent Density Functional Theory with Renormalized Kernels — ●THOMAS OLSEN¹ and KRISTIAN S. THYGESEN² — ¹Universidad del País Vasco — ²Center for Atomic-scale Materials Design (CAMD), Technical University of Denmark

We demonstrate the accuracy of electronic correlation energies obtained from the adiabatic connection and Time-Dependent Density Functional Theory (TDDFT) using a non-empirical renormalized gradient-corrected exchange-correlation kernel. The method can be viewed as a natural step beyond the Random Phase Approximation (RPA) and captures the short-range correlation effects which are poorly described in RPA. In particular, we show that for molecules and solids the renormalized kernel gives a four and five fold improvement in binding energies respectively when compared to RPA. We also consider examples of barrier heights in chemical reactions, molecular adsorption and graphene interacting with metal surfaces, which are three examples where RPA has provided highly accurate results. In these cases, our novel kernel provides results that are of equal quality or even slightly better than RPA, with a similar computational cost. We finally note that the renormalization procedure can be applied to any known semi-local exchange-correlation functional and thus defines an entire new class of adiabatic non-local functionals for ground state calculations within TDDFT.

O 28.6 (402) Tue 12:15 TRE Ma
Low scaling algorithm for the random phase approximation — ●MERZUK KALTAK, JIRI KLIMEŠ, and GEORG KRESSE — University of Vienna, Computational Material Physics

The computationally most expensive step in conventional RPA implementations is the calculation of the independent particle polarizability χ . We present an RPA algorithm that calculates χ using the Green function G in real space and imaginary time. The systematic construction of optimized time and frequency grids for G is obtained by means of solving a fitting problem. Furthermore a non-uniform discrete Fourier transform between the two grids is introduced, which converges exponentially. We show that the usage of the Green function approach in combination with the optimized grids can be used for the calculation of the RPA correlation energy for large systems.

O 28.7 (437) Tue 12:30 TRE Ma
Long range correlation energy from coupled atomic response functions — ●ALBERTO AMBROSETTI and ALEXANDRE TKATCHENKO — Fritz Haber Institut der MPG, Faradayweg 4-6 14195 Berlin, Ger-

many

Electron correlation is an elusive and ubiquitous energy contribution that arises from transient collective electron fluctuations. Its reliable (accurate and efficient) modeling is central to the correct description of cohesive, structural, and response properties of molecules and solids. In this regard, the main challenge is to model the long-range correlation energy beyond (semi-)local density-functional approximations. Here we propose a very efficient method to compute the long-range correlation energy for non-metallic molecules and solids within a density functional theory framework, by using coupled atomic response functions (ARF). Extending the recent MBD method [1], we separate the coupling between ARFs into short and long range, allowing for a seamless many-body treatment of weakly and strongly polarizable systems. Thorough benchmarking on large data sets including small molecules (S22, S66x8), large supramolecular complexes (S12L), molecular crystals (X23) and bulk graphite shows consistently good agreement with high level theoretical and experimental reference binding energies (within the order of 6%). The uniform accuracy for molecules and solids represents a strong validation of our method, and further confirms the importance of modeling the truly collective nature of the long-range correlation energy. [1] A. Tkatchenko et al. PRL **108** 236402 (2012).

O 28.8 (513) Tue 12:45 TRE Ma

The exact Hohenberg-Kohn functional for a lattice model — •TANJA DIMITROV¹, HEIKO APPEL¹, and ANGEL RUBIO^{1,2} — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

Standard local exchange-correlation and semi-local functionals in ground-state density functional theory are known for their shortcomings in describing correct charge transfer, dissociation energies of molecular ions, and barriers of chemical reactions [1,2]. To understand the failures of approximate functionals and to gain insight into the behavior of the exact functional, we investigate the exact solution of the many-body Schrödinger equation for a lattice model. Using exact diagonalization, we explicitly construct the exact Hohenberg-Kohn functional and the mapping from densities to wavefunctions. Besides the normal inter-system derivative discontinuity widely discussed in

the density-functional theory community, we observe a new feature of the exact functional in the low-density limit. This "intra-system derivative discontinuity" resembles the inter-system derivative discontinuity, but is within the system (work in progress [3]). The description of many physical phenomena linked to charge-transfer processes (both in the static and dynamical regimes) require a proper account of this "intra-system derivative discontinuity".

[1] A. J. Cohen et al. Science **321**, 792 (2008).

[2] P. Mori-Sanchez et al., Phys. Rev. Lett. **100**, 146401 (2008).

[3] T. Dimitrov, H. Appel, A. Rubio to be published

O 28.9 (807) Tue 13:00 TRE Ma

Incorporating static correlation effects into density functional theory — NEKTARIOS N. LATHIOTAKIS¹, •NICOLE HELBIG², NIKITAS I. GIDOPOULOS³, and ANGEL RUBIO^{4,5} — ¹Theoretical and Physical Chemistry Institute, NHRF Athens, Greece — ²Peter-Grünberg Institut, Forschungszentrum Jülich, Germany — ³Department of Physics, Durham University, United Kingdom — ⁴Nano-Bio Spectroscopy group, Universidad del País Vasco and DIPC, San Sebastian, Spain — ⁵Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We present a novel idea that builds on the knowledge acquired in Reduced density matrix functional theory (RDMFT) to construct a density-functional scheme which accurately incorporates static and left-right correlation effects. At the same time, the new scheme preserves the high quality of a density functional description at the equilibrium and keeps the computational costs at an acceptable level comparable to the costs when using hybrid functionals. Within this scheme the natural orbitals, i.e. the eigenfunctions of the one-body density matrix, are constrained to be solutions of a single-particle Schrödinger equation with a local effective potential. This provides a natural way to connect an energy eigenvalue spectrum to the natural orbitals. This energy spectrum is found to reproduce the ionization potentials of different atoms and molecules very well. In addition, the dissociation limit of diatomic molecules is well described without the need to break any spin symmetry, i.e. this attractive feature of RDMFT is preserved. The present scheme can be easily implemented in all first principles codes for electronic structure calculations.

O 47: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale IV

Time: Wednesday 10:30–13:15

Location: TRE Ma

Topical Talk O 47.1 (70) Wed 10:30 TRE Ma
From Rydberg Crystals to Bound Magnons - Probing the Non-Equilibrium Dynamics of Ultracold Atoms in Optical Lattices — ●IMMANUEL BLOCH — Max-Planck Institut für Quantenoptik, Garching, Germany — Ludwig-Maximilians-Universität, Munich, Germany

Ultracold atoms in optical lattice form an ideal testbed to probe the non-equilibrium dynamics of quantum many-body systems. In particular recent high-resolution imaging and control techniques allow to probe dynamically evolving non-local correlations in an unprecedented way. As an example, I will focus in my talk on the dynamical excitation of spatially ordered Rydberg structures that are formed through laser excitation from ground state Mott insulating atoms. In addition, I will show how single-spin and spin-pair impurities can be used to directly reveal polaron dynamics in a strongly interacting superfluid or the bound state of two magnons in a Heisenberg ferromagnet - a problem discussed first theoretically more than 80 years ago by H.A. Bethe. New atom interferometric schemes to directly probe the Green's function of a many-body system through the impurity dynamics will be discussed.

O 47.2 (458) Wed 11:00 TRE Ma
Correlated Light-Matter Interactions in Cavity QED — ●JOHANNES FLICK¹, HEIKO APPEL¹, and ANGEL RUBIO^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

In the electronic structure community, the quantized nature of the electrons is usually (approximately) incorporated, whereas the electromagnetic field is mostly treated classically. In contrast, in quantum optics, matter is typically simplified to models with a few levels, while the quantized nature of light is fully explored. In this work, we aim at treating both, matter and light, on an equal quantized footing.

We present exact solutions for fully quantized prototype systems consisting of atoms or molecules placed in optical one- or two-dimensional high-Q cavities and coupled to the quantized electromagnetic modes in the dipole or quadrupole coupling regime. We focus on spontaneous emission, strong-coupling phenomena, dipole-dipole couplings including van-der-Waals interactions, and Förster resonance energy transfer (FRET), all beyond the rotating-wave approximation.

This work has implications for a future development of a time-dependent density functional theory formulation of QED [1,2] for correlated multi-photon configurations.

[1] M. Ruggenthaler, F. Mackenroth, and D. Bauer, Phys. Rev. A **84**, 042107 (2011).

[2] I. Tolkatly, Phys. Rev. Lett. **110**, 233001 (2013).

O 47.3 (578) Wed 11:15 TRE Ma
Optimized effective potential approach to time-dependent density functional theory for many-electron systems interacting with cavity photons — ●CAMILLA PELLEGRINI¹, JOHANNES FLICK², HEIKO APPEL², ILYA V. TOKATLY^{1,3}, and ANGEL RUBIO^{1,2} — ¹Nano-bio Spectroscopy Group and ETSF Scientific Development Centre, Departamento de Física de Materiales, Universidad del País Vasco UPV/EHU, E-20018 San Sebastián, Spain — ²Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — ³IKERBASQUE, Bilbao, Spain

In a recent paper [1] time dependent density functional theory has been generalized to many-electron systems strongly coupled to quantum electromagnetic modes of a microcavity. Here we construct an approximation for the corresponding exchange-correlation (xc) potential by extending the optimized effective potential (OEP) method to the electron-photon system. The derivation of the OEP equation employing the non-equilibrium Green's function formalism, and the first order approximation for the electronic self-energy is presented. Beyond the mean field level, the electron-photon coupling generates a time non-local photon-mediated interaction between the electrons, whose propagator enters the exchange-like diagram. We further show the approximated xc-potential for a model two-level diatomic molecule with one electron coupled to photon modes. The comparison between the

obtained results and the exact numerical ones in the different coupling regimes (from weak up to ultra-strong) is discussed. [1] I.V. Tokatly, Phys. Rev. Lett. **110**, 233001(2013)

O 47.4 (727) Wed 11:30 TRE Ma
Correlated photon-electron wavefunctions in cavity Quantum Electrodynamics — ●HEIKO APPEL¹, JOHANNES FLICK¹, RENE JESTAEDT¹, and ANGEL RUBIO^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

Experimental progress in recent years has enabled the fabrication of Fabry-Perot resonators with high optical quality factors (high-Q). Such cavities allow to study the interaction of matter with a quantized light field at the single-photon level (Nobel prize 2012). In this talk we present the real-time evolution of correlated photon-electron wavefunctions in optical one- and two-dimensional high-Q cavities. We discuss implications for a multi-component density functional theory for Quantum Electrodynamics [1,2] based on the time-dependent electron density and the photon energy density.

[1] M. Ruggenthaler, F. Mackenroth, and D. Bauer, Phys. Rev. A **84**, 042107 (2011).

[2] I. Tolkatly, Phys. Rev. Lett. **110**, 233001 (2013).

O 47.5 (242) Wed 11:45 TRE Ma
Photoelectron driven plasmaron excitations in (2x2)K/Graphite — ●BO HELLSING — Department of Physics, Gothenburg University, Sweden

A new type of plasmarons formed by the compound of photoelectrons and acoustic surface plasmon (ASP) excitations is investigated in the system p(2 × 2)-K/Graphite. The physics behind these types of plasmarons, e-plasmarons, is different from the ones recently found in graphene and quantum well systems, where the loss features results from the photohole-plasmon interaction in the material, h-plasmarons. Based on the first principles scheme, Time dependent density functional (TDDFT), we calculated the linear response due to the presence of the escaping photo-electron and determine the ASP dispersion. The coupling between the photoelectron and the ASP gives rise to excitation of the e-plasmarons manifested by a broad dispersive feature shifted about 0.5 eV below parabolic K induced quantum well band (QWB) in agreement with the ARPES experiment by Agdal et al. The e-plasmarons should be considered as a source of the loss satellite structure in ARPES for 2D systems. In addition they are important to take into account in theoretical studies of different compounds as they reflect an additional channel for excitations of plasmons. This could then increase the photon-plasmon conversion yield which obviously is of interest in the field of plasmonics.

O 47.6 (253) Wed 12:00 TRE Ma
Charge-transfer excitations in organic systems from many-body perturbation theory — ●XAVIER BLASE¹, CARINA FABER^{1,2}, PAUL BOULANGER¹, CLAUDIO ATTACCALITE¹, and IVAN DUCHEMIN² — ¹Institut Néel, CNRS and UJF, Grenoble, France — ²L.SIM/INAC, CEA, Grenoble, France

Charge-transfer excitations in organic systems lies at the heart of a large variety of physical phenomena, from photosynthesis to photovoltaics, photocatalysis or DNA denaturation. From a theoretical point of view, such nonlocal excitations are well known to lead to difficulties within the TDDFT framework, leading to the development of range-separated hybrids. We present here the merits of the Bethe-Salpeter formalism and demonstrate its ability to reproduce *cold* and *hot* Frenkel or charge-transfer excitations with remarkable accuracy [1-3]. Our calculations are based on a recent Gaussian basis implementation of the GW and Bethe-Salpeter formalism, the Fiesta initiative [1-4], allowing all-electron or pseudopotential excited states calculations for systems comprising several hundred atoms. Recent developments towards discrete and continuous embedding techniques within the many-body perturbation framework will be presented.

References: [1] C. Faber, I. Duchemin, T. Deutsch, X. Blase, Phys. Rev. B, **86**, 155315 (2012). [2] I. Duchemin, T. Deutsch, X. Blase, Phys. Rev. Lett. **109**, 167801 (2012). [3] I. Duchemin and X. Blase,

Phys. Rev. B 87, 245412 (2013). [4] X. Blase, C. Attaccalite, V. Olevano, Phys. Rev. B 83, 115103 (2011).

O 47.7 (256) Wed 12:15 TRE Ma

Charge transfer from first principles: self-consistent GW applied to donor-acceptor systems — ●FABIO CARUSO^{1,2}, VIKTOR ATALLA¹, ANGEL RUBIO^{1,3}, MATTHIAS SCHEFFLER¹, and PATRICK RINKE¹ — ¹Fritz Haber Institute, Berlin, Germany — ²University of Oxford, UK — ³Universidad del País Vasco, San Sebastián, Spain

Charge transfer in donor-acceptor systems (DAS) is determined by the relative alignment between the frontier orbitals of the donor and the acceptor. Semi-local approximations to density functional theory (DFT) may give a qualitatively wrong level alignment in DAS, if the ionisation potential of one molecule erroneously ends up above the electron affinity of the other. An unphysical fractional electron transfer will then result in weakly interacting DAS [1]. GW calculations based on first-order perturbation theory (G_0W_0) correct the level alignment. However, the ground state is unaffected by the G_0W_0 approach, and the charge-transfer properties remain on the level of the initial DFT calculation [1]. We demonstrate that self-consistent GW (scGW) – based on the iterative solution of the Dyson's equation – provides an ideal framework for the description of charge transfer in DAS. The scGW level alignment is in agreement with experimental reference data. In addition ground- and excited-state properties are described at the same level of theory. As a result, the electron density in DAS is consistent with the level alignment between donor and acceptor, leading to a qualitatively correct description of charge-transfer properties.

[1] V. Atalla, M. Yoon, F. Caruso, P. Rinke, and M. Scheffler, Phys. Rev. B 88, 165122 (2013).

O 47.8 (391) Wed 12:30 TRE Ma

What Koopmans' compliant orbital-density dependent functionals can do for you: a comprehensive benchmark of the G2-set — ●GIOVANNI BORCHI¹, NGOC LINH NGUYEN¹, ANDREA FERRETTI², ISMAILA DABO³, and NICOLA MARZARI¹ — ¹École Polytechnique Fédérale de Lausanne, Lausanne (VD), CH — ²Centro S3, CNR-NANO, Modena, IT — ³Department of Materials Science and Engineering, Penn State University, University Park (PA), USA

In this talk we present the results of benchmark calculations of the structure and electronic-structure of all molecules in the g2 set, using different flavours for Koopmans' compliant (KC) functionals. Results are compared not only to LDA and PBE, but also to orbital-density dependent calculations with the Perdew-Zunger self-interaction correction.

Our results assess the accuracy of Koopmans' compliant functionals in improving semilocal functionals to predict electronic eigenvalues and in particular ionization energies, with an accuracy that for molecules seems to be comparable or superior to that of many-body (GW) approaches. We also highlight how the Koopmans' condition tends to preserve the potential energy surface of the underlying functional, with higher reliability than e.g. PBE in structural predictions, while also providing good estimates of atomization energies.

The talk will also provide a general introduction to the theory of Koopmans' compliant functionals and their implementation in existing electronic structure codes.

Ref. Dabo *et al.*, PRB 82, 115121 (2010), and Psik highlight (2012).

O 47.9 (526) Wed 12:45 TRE Ma

The electronic structure of quinacridone: Optimally tuned range-separated hybrid functional versus GW results — DANIEL LÜFTNER¹, SIVAN REFAELY-ABRAMSON², MICHAEL PACHLER¹, MICHAEL G. RAMSEY¹, LEEOR KRONIK², and ●PETER PUSCHNIG¹ — ¹Institut für Physik, Karl-Franzens-Universität Graz, Austria — ²Department of Materials and Interfaces, Weizmann Institute of Science, Israel

Quinacridone is an organic molecule (C₂₀H₁₂N₂O₂) utilized in the formation of organic pigments. It has also been discussed for usage in organic electronics particularly due to its stability under ambient conditions and its tendency to form self-assembled supramolecular networks. Here, we report on its electronic structure, both, for the isolated molecule as well as for the alpha- and beta- bulk molecular crystal polymorphs. We employ an optimally tuned range-separated hybrid functional (OT-RSH) within density functional theory as well as GW corrections within a many-body perturbation theory framework. A comparison of the theoretical results obtained with the different levels of theory and a subsequent comparison with experimental data from angle-resolved photoemission spectroscopy emphasize the need for going beyond simple semi-local DFT-functionals in order to obtain the correct orbital ordering. Furthermore the comparison indicates that the results obtained with OT-RSH greatly improve those of standard DFT functionals and achieve an agreement with experiment at the level of GW calculations, thus making the OT-RSH an alternative to the computationally more expensive GW approach.

O 47.10 (191) Wed 13:00 TRE Ma

GW many-body perturbation theory for electron-phonon coupling calculations — ●CARINA FABER^{1,2}, PAUL BOULANGER¹, IVAN DUCHEMIN^{1,2}, and XAVIER BLASE¹ — ¹Institut Néel, CNRS, Grenoble, France — ²INAC, CEA, Grenoble, France

We study within many-body perturbation theory the electron-phonon coupling in organic systems, taking as paradigmatic examples the fullerene molecule and the pentacene crystal [1,2]. We show that the strength of the electron-phonon coupling potential is dramatically underestimated at the LDA level, while GW calculations offer an excellent agreement with experiments [1]. Further, combining GW calculations of the electronic band structure and of the electron-phonon coupling in crystalline pentacene, we show that the hole bands dispersion can be reconciled with photoemission experiments, by solving non-perturbatively (DMFT) the effect of electron-phonon coupling on the electronic self-energy [2]. We finally explore various approximations that may allow to combine the GW formalism with convenient linear response formalisms beyond the frozen-phonon techniques. Our calculations are performed with the Fiesta package, a Gaussian based GW and Bethe-Salpeter code allowing all-electron or pseudopotential calculations with various resolution of the identity techniques and without any plasmon pole approximation [3,4].

[1] C. Faber *et al.*, Phys. Rev. B 84, 155104 (2011) [2] S. Ciuchi *et al.*, Phys. Rev. Lett. 108, 256401 (2012) [3] C. Faber, I. Duchemin, T. Deutsch, X. Blase, Phys. Rev. B, 86, 155315 (2012). [4] I. Duchemin, T. Deutsch, X. Blase, Phys. Rev. Lett. 109, 167801 (2012).

O 56: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale V

Time: Wednesday 16:00–19:15

Location: TRE Ma

Topical Talk

O 56.1 (73) 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.

O 56.2 (634) 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).

O 56.3 (324) 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).

O 56.4 (574) 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

O 56.5 (573) 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.

O 56.6 (659) 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.

O 56.7 (670) 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.

O 56.8 (677) 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).

O 56.9 (175) 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).

O 56.10 (688) 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).

O 56.11 (773) 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.

O 70: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale VI

Time: Thursday 10:30–13:15

Location: TRE Ma

Topical Talk O 70.1 (69) Thu 10:30 TRE Ma
Localization at the edge of 2D topological insulator by Kondo impurities — ●BORIS ALTSHULER¹, IGOR ALEINER¹, and VLADIMIR YUDSON² — ¹Physics Department, Columbia University, New York, NY 10027, USA — ²Institute for Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow 142190, Russia

Recent interest to the topological insulators [1] is inspired by the fact that their boundaries host gapless electronic excitations, which are extended and make the system conductive even in the presence of a potential disorder. 1D edge of a 2D topological insulator is predicted to have perfect conductance ($2e^2/h$): right and left moving electrons carry opposite spins and potential disorder cannot flip spins and thus causes neither back-scattering nor the usual 1D localization.

What if there are localized spins coupled to the edge electrons? It turns out that the conductivity is still perfect provided that this coupling conserves the z-projection of the total spin of the impurities and electrons. Magnetic anisotropy violates this conservation and causes the backscattering even at $T=0$, i.e. an arbitrary small density of the spins with arbitrary weak anisotropy of the coupling leads to Anderson localization of the edge states in long enough samples [3]. The conclusion follows from the mapping of the electron-spin coupling to the well-studied problem [2] of disordered Luttinger liquid.

1. M.Z. Hasan and C.L. Kane, Rev. Mod. Phys. 82, 3045 (2010).
2. T.Giamarchi and H.J.Schulz, Phys. Rev. B 37, 325 (1988).
3. B.L.Altshuler, I.L.Aleiner, V.I. Yudson Phys. Rev. Lett 111, 086401 (2013)

O 70.2 (496) Thu 11:00 TRE Ma
Multiple Exciton Generation in Si and Ge Nanoparticles with high pressure core structures — ●STEFAN WIPPERMANN¹, MARTON VÖRÖS², DARIO ROCCA³, ADAM GALI⁴, GERGELY ZIMANYI², and GIULIA GALLI² — ¹Max-Planck-Institute for Iron Research, Düsseldorf — ²University of California, Davis — ³Universite de Lorraine, Nancy — ⁴Budapest University of Technology and Economics

Multiple exciton generation (MEG) in semiconductor nanoparticles (NPs) is a promising path towards surpassing the Shockley-Queisser limit in solar energy conversion efficiency. Recent studies demonstrate MEG to be more efficient in NPs than in the bulk, including Si. However, the increased efficiency is observed only on a relative energy scale in units of the gap: quantum confinement (QC) effects believed to be responsible for efficient MEG in NPs, also increase their optical gap, swiftly shifting the MEG threshold beyond the solar spectrum.

We present density functional and many body perturbation theory calculations of the electronic, optical, and impact ionization properties of Si and Ge nanoparticles (NPs) with core structures based on high-pressure bulk Si and Ge phases. Si and Ge particles with a BC8 or ST12 core structure exhibit significantly lower optical gaps and multiple exciton generation (MEG) thresholds, and an order of magnitude higher MEG rate than diamondlike ones of the same size (1).

- (1) S. Wippermann et al., Phys. Rev. Lett. 110, 046804 (2013)

O 70.3 (518) Thu 11:15 TRE Ma
Advanced time-evolution method for optical absorption spectra calculations — ●TOBIAS SANDER and GEORG KRESSE — Computational Materials Physics, University of Vienna, Sensengasse 8/12, 1090 Vienna, Austria

The Green's function formalism from many-body perturbation theory gives access to electronic structure calculation within the quasiparticle picture, as well as provides for calculating optical absorption spectra. Within the traditional ansatz [1], a Bethe-Salpeter like equation for the polarizability is solved. This requires to diagonalize an in general non-hermitian and complex matrix (BSE matrix). Usually, the off-diagonal elements of the BSE matrix are neglected and this is referred to as Tamm-Dancoff approximation. The computational effort can be reduced by using the time-evolution ansatz [2] which avoids the matrix diagonalization. We present a method based on the time-evolution algorithm, that finally avoids storing and diagonalizing the BSE matrix. This leads to a reduction of the scaling w.r.t the system size N from N^5 to N^3 . Finally, we present first results for typical systems.

- [1] S. Albrecht, L. Reining, R. Del Sole, G. Onida, PRL 80, 4510

(1998)
 [2] W. G. Schmidt, S. Glutsch, P. H. Hahn, F. Bechstedt, PRB 67, 085307 (2003)

O 70.4 (586) Thu 11:30 TRE Ma
New starting point for the calculation of optical properties — ●IGOR RESHETNYAK^{1,2} and LUCIA REINING^{1,2} — ¹Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France — ²European Theoretical Spectroscopy Facility (ETSF)

The Bethe-Salpeter Equation based on Hedin's GW approximation to the self-energy is a powerful approach for describing electron-hole interactions in optical properties and photo-absorption spectra. However, in its current formulation it is both computationally heavy and displays cancellation effects not accounted for analytically. We discuss the sources of these cancellations and the possibility of putting them forward explicitly. We furthermore assess alternative formulations and sets of approximations to the BSE. For each of them we examine its behavior on model systems as well as their computational applicability. Finally we suggest possible directions for further investigations.

O 70.5 (399) Thu 11:45 TRE Ma
Electron-Energy Loss and Inelastic X-ray Scattering of CuO from First Principles — ●CLAUDIA RÖDL, FRANCESCO SOTTILE, MATTEO GATTI, and LUCIA REINING — Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau cedex, France and European Theoretical Spectroscopy Facility (ETSF)

Even though the strongly correlated transition-metal oxide CuO has many fields of application (potential absorber material in photovoltaic devices, pigment in glass and ceramics, building block of cuprate superconductors,...), surprisingly little is known about its electronic excitations from a theoretical point of view. The band gap and all electronic excitations in its vicinity are governed by the intricate interplay between itinerant $O\ 2p$ and localized $Cu\ 3d$ electrons. Complex many-body effects, that are still not well understood nowadays, determine the screening of the electron-electron interaction.

Electron-energy loss and inelastic x-ray scattering experiments yield direct access to the wave-vector- and frequency-dependent loss function $-\text{Im}\ \varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, \omega)$, and, hence, to the screened Coulomb interaction W . We use time-dependent density-functional theory (TDDFT) to calculate the loss spectrum of CuO and discuss the occurring $d-d$ and plasmon excitations. This allows us, by comparing theory and experiment, to assess the quality of the screened Coulomb interaction which is a key quantity for many-body approaches, for instance, GW and Bethe-Salpeter calculations.

O 70.6 (460) Thu 12:00 TRE Ma
Optical Spectra from Molecules to Solids: Insight from Many-Body Perturbation Theory — ●CATERINA COCCHI and CLAUDIA DRAXL — Humboldt-Universität zu Berlin, Institut für Physik and IRIS Adlershof, Berlin, Germany

The spurious long-range behavior of time-dependent (TD) density functional theory (DFT) is a well known source of error in describing bound excitons in solids. Remarkably, TD-DFT is often able to capture the optical features of isolated systems, even with the most simple exchange-correlation kernels, like the TD local density approximation. With the example of molecular crystals, we aim at solving the puzzle when and why TD-DFT can be relied on. We answer this question by confronting TD-DFT with many-body perturbation theory (GW and Bethe-Salpeter equation), which is the most accurate methodology to describe optical excitations in solids. Our results are obtained with the all-electron code "exciting" (<http://exciting-code.org>), where all the quantities entering the two formalisms are treated on the same footing [1]. In-depth analysis allows us to identify the shortcomings of TD-DFT in predicting the excitonic spectra of extended systems and to understand when this methodology is capable of providing correct results.

- [1] S. Sagmeister and C. Draxl, Phys. Chem. Chem. Phys. 11, 4451 (2009)

O 70.7 (481) Thu 12:15 TRE Ma

Relativistic Solar Cells — ●PAOLO UMARI¹, EDOARDO MOSCONI², and FILIPPO DE ANGELIS² — ¹Dipartimento di Fisica e Astronomia, Università di Padova, via Marzolo 8, I-35131 Padova, Italy — ²Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, I-06123, Perugia, Italy

Hybrid AMX₃ perovskites (A=Cs, CH₃NH₃; M=Sn, Pb; X=halide) have revolutionized the scenario of emerging photovoltaic technologies. Indeed, a rapid evolution led, very recently, up to 15% efficient solar cells. CH₃NH₃PbI₃ has so far dominated the field, while the similar CH₃NH₃SnI₃ has not been explored for photovoltaic applications, despite the reduced band-gap. Replacement of Pb by the more environment-friendly Sn would facilitate the large uptake of perovskite-based photovoltaics. Despite the extremely fast progress, the materials electronic properties which are key to the photovoltaic performance are relatively little understood. Here we develop an effective GW method incorporating spin-orbit coupling which allows us to accurately model the electronic, optical and transport properties of CH₃NH₃SnI₃ and CH₃NH₃PbI₃, opening the way to new materials design. The different CH₃NH₃SnI₃ and CH₃NH₃PbI₃ properties are discussed in light of their exploitation for solar cells, and found to be entirely due to relativistic effects.

O 70.8 (506) Thu 12:30 TRE Ma

Solar nanocomposites with complementary charge extraction pathways for electrons and holes: Si embedded in ZnS — ●STEFAN WIPPERMANN¹, MARTON VÖRÖS², ADAM GALI³, FRANCOIS GYGI², GERGELY ZIMANYI², and GIULIA GALLI² — ¹Max-Planck-Institute for Iron Research, Düsseldorf — ²University of California, Davis — ³Budapest University of Technology and Economics

We propose that embedding silicon nanoparticles (NP) into amorphous, non-stoichiometric ZnS leads to promising nanocomposites for solar energy conversion. Using *ab initio* molecular dynamics simulations we show that upon high temperature amorphization of the host chalcogenide, sulfur atoms are drawn to the NP surface. We found that the sulfur content may be engineered to form a type II heterojunction, with complementary charge transport channels for electrons and holes, and that sulfur capping is beneficial to lower the nanoparticle gap, with respect to that of NPs embedded in oxide matrices. Our analysis was conducted using density functional theory with local and hybrid functionals and many body perturbation theory at the GW level.

O 70.9 (568) Thu 12:45 TRE Ma

Ultraviolet photo-emission spectroscopies from Koopmans-compliant functionals — ●NGOC LINH NGUYEN¹, GIOVANNI BORGHI¹, ANDREA FERRETTI², ISMAILA DABO³, and NICOLA MARZARI¹ — ¹Theory and Simulations of Materials, École Polytechnique

Fédérale de Lausanne, Station 12, 1015 Lausanne, Switzerland. — ²Centro S3, CNR-Istituto Nanoscienze, I-41125 Modena, Italy — ³Department of Materials Science and Engineering, The Pennsylvania State University, University Park, USA.

We study the photo-electron properties of organic photovoltaic molecules using Koopmans-compliant functionals [1] as well as the Perdew-Zunger self-interaction correction (PZ-SIC) [2] to density-functional theory. A simple method for simulating ultraviolet photo-emission spectra (UPS) of molecules has been implemented. It is based on a plane-wave approximation for the final states to account for the spectra intensities. Our calculations show that Koopmans-compliant functionals provide ionization potentials and electron affinities closely comparable with those obtained by many-body perturbation theory (GW). In addition, we find that UPS spectra computed imposing the Koopmans' condition on the PZ-SIC functional are in remarkable agreement with experimental results.

Refs: [1] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, and M. Cococcioni, *Phys. Rev. B* 82, 115121 (2010); [2] J. P. Perdew and A. Zunger, *Phys. Rev. B* 23, 5048 (1981).

O 70.10 (795) Thu 13:00 TRE Ma

Self-consistent dynamical embedding in real space — ●Wael Chibani¹, XINGUO REN^{1,2}, PATRICK RINKE¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²Key Laboratory of Quantum Information, USTC, Hefei, China

Density-functional theory with its local-density (LDA) and generalized gradient approximations (GGA) is known to fail for localized states. To extend *ab initio* approaches to this domain, we have devised an embedding scheme that facilitates the treatment of the physically important part of a system with electronic structure methods, that are computationally too expensive for periodic systems, whereas the rest of the periodic system is treated with computationally less demanding approaches, i.e. LDA/GGA, in a self-consistent manner. Our scheme is based on the concept of dynamical mean-field theory (DMFT) [1]. However, in contrast to the original DMFT formulation for correlated model Hamiltonians, we consider here the unit cell as embedded cluster in an *ab initio* way, that includes all electronic degrees of freedom. The performance of our scheme is demonstrated by treating the embedded region with hybrid functionals for simple bulk systems, e.g. Si or NiO. The total energy and the density of states converge rapidly with respect to the computational parameters and approach their bulk limit with increasing cluster size. By treating the embedded region with GW we were able to improve the band gap using only a small cluster. The effect of self-consistency in GW for the embedded region will also be addressed. [1] A. Georges *et al.*, *Rev. Mod. Phys.* **68**,14 (2006)