

Symposium Frontiers of Electronic Structure Theory: Many-body Effects on the Nano-Scale (SYME)

jointly organized by
the Semiconductor Physics Division (HL),
the Chemical and Polymer Physics Division (CPP),
the Metal and Material Physics Division (MM),
the Surface Science Division (O), and
the Low Temperature Physics Division (TT)

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The progress in semiconductor- and metal-based nanotechnology gave access to unprecedented control of many-body effects in small systems from macro-molecules to mesoscopic structures. A particular focus of the Symposium is to bring the predictive and descriptive power of modern electronic-structure theory closer to experimental work in semiconductor physics, surface science, magnetism, and chemical physics.

The Symposium “Frontiers of Electronic Structure Theory” is completed by six joint sessions hosted by the Surface Science Division including six Invited Talks and more than 50 Contributed Talks.

Overview of Invited Talks and Sessions

(Lecture room: H 0105)

Invited Talks

SYME 1.1	Fri	9:30–10:00	H 0105	Excitations and charge transfer phenomena in C based systems — •ELISA MOLINARI
SYME 1.2	Fri	10:00–10:30	H 0105	Towards optimal correlation factors for many-electron perturbation theories — •ANDREAS GRÜNEIS
SYME 1.3	Fri	10:30–11:00	H 0105	Towards an ab-initio description of high temperature superconductivity — •GARNET CHAN
SYME 1.4	Fri	11:15–11:45	H 0105	Correlation effects in unconventional superconductors: from micro- to nano- and macroscales. — •ROSER VALENTI
SYME 1.5	Fri	11:45–12:15	H 0105	Stochastic density functional and GW theories scaling linearly with system size — •ROI BAER, DANIEL NEUHAUSER, ERAN RABANI

Sessions

SYME 1.1–1.5	Fri	9:30–12:15	H 0105	Frontiers of Electronic Structure Theory: Many-body Effects on the Nano-scale
SYME 2.1–2.11	Tue	10:30–13:30	MA 004	Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale I
SYME 3.1–3.6	Tue	14:00–15:45	MA 004	Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale II
SYME 4.1–4.11	Wed	10:30–13:30	MA 004	Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale III
SYME 5.1–5.13	Wed	15:00–18:30	MA 004	Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale IV
SYME 6.1–6.10	Thu	10:30–13:15	MA 004	Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale V
SYME 7.1–7.13	Thu	15:00–18:30	MA 004	Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale VI

SYME 1: Frontiers of Electronic Structure Theory: Many-body Effects on the Nano-scale

Time: Friday 9:30–12:15

Location: H 0105

Invited Talk SYME 1.1 Fri 9:30 H 0105
Excitations and charge transfer phenomena in C based systems — ●ELISA MOLINARI — University of Modena and Reggio Emilia, Modena, Italy — CNR, Istituto Nanoscienze, Modena, Italy

Excitonic effects control excitations and optical spectra in graphene-based nanostructures and related polymers [1], as well as in interacting C-based molecular systems of relevance for photovoltaics [2]. I will show results from ab-initio many body perturbation theory and discuss their implications for spectroscopies and for a realistic description of ultrafast charge separation phenomena.

[1] R. Denk et al, Nat Commun 5, 4253 (2014); A. Batra et al, Chem Sci 5, 4419-4423 (2014); L. Massimi et al, J. Phys. Chem C, in press.
 [2] S. M. Falke et al, Science 344, 1001-1005 (2014).

Invited Talk SYME 1.2 Fri 10:00 H 0105
Towards optimal correlation factors for many-electron perturbation theories — ●ANDREAS GRÜNEIS — Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany — Universität Wien, Vienna, Austria

Many electron perturbation theories such as the coupled-cluster method form a hierarchy of increasingly accurate approximations to the electronic ground state wave function. This presentation will overview recent progress in applying coupled-cluster methods to solids and techniques to reduce their computational cost such as explicit correlation methods [1,2]. Furthermore applications to archetypal solid state systems as well as the uniform electron gas model system will be discussed [3].

[1] G. H. Booth, A. Grüneis, G. Kresse and A. Alavi, Nature 493, 365-370 (2013).

[2] A. Grüneis, J.J. Shepherd, A. Alavi, D.P. Tew, G.H. Booth, The Journal of chemical physics 139 (8), 084112 (2013).

[3] J.J. Shepherd, A. Grüneis, Physical Review Letters 110 (22), 226401 (2013).

Invited Talk SYME 1.3 Fri 10:30 H 0105
Towards an ab-initio description of high temperature superconductivity — ●GARNET CHAN — Department of Chemistry, Princeton University, United States NJ08544

I will describe our continued efforts in developing ab-initio many-body theory in the condensed phase with a view to a first principles description of a cuprate phase diagram.

Coffee break

Invited Talk SYME 1.4 Fri 11:15 H 0105
Correlation effects in unconventional superconductors: from micro- to nano- and macroscales. — ●ROSER VALENTI — Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1, 60438 Frankfurt am Main, Germany

The combination of ab initio density functional theory with dynamical mean field theory (DFT+DMFT) has been proven to be a powerful approach for describing correlation effects in solid state systems at the microscopic level. In this talk we will focus on recent progress on this method and its application to unconventional superconductors such as Fe-pnictides, organic charge-transfer salts as well as correlated Dirac metals [1,2,3]. Further, we shall discuss the manifestation of such effects at the nano- and macroscales.

[1] I. I. Mazin *et al.* Nature Communications 5, 4261 (2014)

[2] S. Backes *et al.* New J. Phys. 16, 083025 (2014)

[3] J. Ferber *et al.* Phys. Rev. B 89, 205106 (2014)

Invited Talk SYME 1.5 Fri 11:45 H 0105
Stochastic density functional and GW theories scaling linearly with system size — ●ROI BAER¹, DANIEL NEUHAUSER², and ERAN RABANI³ — ¹Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, 91904 Israel. — ²Department of Chemistry and Biochemistry, University of California, Los Angeles Los Angeles, CA 90095-1569 USA. — ³Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720 USA.

Kohn-Sham density functional theory (KS-DFT) is formulated as a statistical theory in which the electron density is determined from an average of correlated stochastic densities in a trace formula. Method allows reliable estimates of the electronic band structure, forces on nuclei, density and moments etc. "Self-averaging" leads to sublinear scaling. An embedded fragment stochastic DFT greatly decreases statistical fluctuations. Based on stochastic DFT a GW method is developed scaling linearly with system size. We demonstrate the results on silicon nanocrystals and large water clusters. References: *Phys. Rev. Lett. 111, 106402 (2013). *Phys. Rev. Lett. 113, 076402 (2014). *J. Chem. Phys. 141, 041102 (2014).

SYME 2: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale I

Time: Tuesday 10:30–13:30

Location: MA 004

Invited Talk SYME 2.1 Tue 10:30 MA 004
Electronic structure in the vicinity of strong non-adiabatic couplings — ●EBERHARD K.U. GROSS — Max Planck Institute of Microstructure Physics, Halle (Saale), Germany

The Born-Oppenheimer (BO) approximation is among the most fundamental ingredients of modern Condensed-Matter Theory. Yet, some of the most fascinating phenomena such as the process of vision or phonon-driven superconductivity occur in the regime where the BO approximation breaks down. To tackle such situations one has to face the Hamiltonian of the complete system of interacting electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration. The resulting equations of motion for the nuclear and electronic wavefunctions lead to a unique definition of exact potential energy surfaces as well as exact geometric phases. We show an example [2] where the geometric phase associated with the conical intersection of BO surfaces has no counterpart in the true electron-nuclear wavefunction. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3], reminiscent of Tully surface hopping algorithms. Based on this observation we propose novel mixed-quantum-classical algorithms.

[1] Abedi, Maitra, Gross, PRL 105, 123002 (2010).

[2] Min, Abedi, Kim, Gross, PRL 113, 263004 (2014).

[3] Abedi, Agostini, Suzuki, Gross, PRL 110, 263001 (2013).

SYME 2.2 Tue 11:00 MA 004
Towards First-Principles Modeling of Electrolytic Solvent Effects in Photo-Catalytic Water Splitting — ●STEFAN RINGE¹, SEBASTIAN MATERA², HARALD OBERHOFER¹, and KARSTEN REUTER¹ — ¹Technische Universität München — ²Freie Universität Berlin

Due to the complexity of the physical processes underlying photo-catalytic surface reactions, ab-initio computational approaches have to overcome major challenges concerning accuracy and computational costs. In particular, an efficient description of electrolytic solvent effects—which are crucial for charge driven reactions—is highly necessary.

We present an implementation of the modified Poisson-Boltzmann (MPB) model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. In contrast to most implicit solvent models, this technique combines nonlinear dielectric solvent response with a statistical description of solvated finite-sized ions. This has been shown to capture a majority of electrochemical solvent effects appearing in heterogeneous photo-catalysis.[1]

We developed a self-consistent function-space oriented solution scheme for Poisson-Boltzmann-like equations which in contrast to com-

mon multi-grid solvers is able to exploit the specialized grids and optimized integration schemes of FHI-aims. We demonstrate the approach and its efficiency for the linearized Poisson-Boltzmann equation and a range of molecular systems. Finally, we discuss how the methodology can be employed for the solution of non-linear problems. [1] Kilic, M.S., Bazant, M.Z., *Phys. Rev. E*, **75**, **2007**, 021502.

SYME 2.3 Tue 11:15 MA 004

Phonons in Molecular Crystals: The Role of Collective van der Waals Interactions — ●JOHANNES HOJA and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

By now, it is well established that dispersive van der Waals (vdW) interactions are crucial for the structure and stability of molecular crystals [1]. However, complete understanding of functionality of molecular crystals also requires a predictive description of response to external perturbations. Here we study the role of vdW interactions on phonons in molecular crystals. This subject is important since such low-frequency vibrations can be used to identify for instance drugs, explosives, and different polymorphic forms of molecular crystals. We studied the vibrational spectra of several molecular crystals with density-functional theory, including many-body dispersion interactions (DFT+MBD method). We find that long-range MBD effects can give rise to novel peaks in the phonon density of states [2], which can not be observed with a simple pairwise treatment of vdW interactions. We further discuss the nature of these vibrations and demonstrate a non-trivial connection between collective vdW interactions and entropy of molecular crystals.

[1] L. Kronik, A. Tkatchenko, *Acc. Chem. Res.* **47**, 3208 (2014).

[2] A. M. Reilly, A. Tkatchenko, *Phys. Rev. Lett.* **113**, 055701 (2014).

SYME 2.4 Tue 11:30 MA 004

Converged Nuclear Quantum Statistics from Semi-Classical Path Integrals — ●IGOR POLTAVSKIY and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The quantum nature of nuclear motions plays a vital role in the structure, stability, and thermodynamics of molecular systems. The standard approach to take nuclear quantum effects (NQE) into account is the Feynman-Kac imaginary-time path-integral molecular dynamics (PIMD). Conventional PIMD simulations require exceedingly large number of classical subsystems (beads) to accurately capture NQE, resulting in considerable computational cost even at room temperature due to the rather high internal vibrational frequencies of many molecules of interest.

We propose a novel parameter-free form for the PI partition function and estimators to calculate converged thermodynamic averages. Our approach requires the same ingredients as the conventional PIMD simulations, but decreases the number of required beads by roughly an order of magnitude. This greatly extends the applicability of *ab initio* PIMD for realistic molecular systems. The developed method has been applied to study the thermodynamics of N₂, H₂O, CO₂, and C₆H₆ molecules. For all of the considered systems at room temperature, 4 to 8 beads are enough to recover the NQE contribution to the total energy within 2% of the fully converged quantum result.

SYME 2.5 Tue 11:45 MA 004

Can we get reliable quantum dynamics simulations for vibrational spectra in the condensed phase? — ●MARIANA ROSSI¹, DAVID MANOLOPOULOS¹, and MICHELE CERIOTTI² — ¹University of Oxford, Oxford, UK — ²EPFL, Lausanne, Switzerland

At the level of accuracy we can now achieve in first-principles calculations, the inclusion of more subtle nuclear quantum effects (NQE) in simulations become more relevant. However, their inclusion is challenging for anharmonic and dynamical processes, in particular in the condensed phase. We show a new method to approximate quantum corrections in time-dependent properties based on a path integral framework, called thermostatted ring polymer molecular dynamics (TRPMD) [1], which is immune to pathological problems of previously proposed methods. We perform a systematic comparison of TRPMD with other approaches that rely on different approximations to quantum dynamics, to assess their performance for the IR spectrum of HOD in D₂O and water at different phases/temperatures [2]. Using an empirical potential energy surface (q-TIP4P/f), we find that the different techniques are largely consistent with one another, within a few tens of cm⁻¹. Comparison with classical molecular dynamics demonstrates the importance of NQE even up to 600K. The cross validation between

these different approaches provides clues to limitations of their underlying approximations and paves the way for more reliable approaches to nuclear quantum dynamics that are feasible together with electronic structure methods. [1] M. Rossi, M. Ceriotti, D. Manolopoulos, *JCP* **140**, 234116 (2014); [2] M. Rossi, et al., *JCP* **141**, 181101 (2014)

SYME 2.6 Tue 12:00 MA 004

Ultra-high temperature properties of ZrC: a fully-anharmonic ab-initio approach — ●ANDREW DUFF¹, DOMINIQUE KORBMACHER², ALBERT GLENSK², BLAZEJ GRABOWSKI², JOERG NEUGEBAUER², and MIKE FINNIS¹ — ¹Department of Physics and Department of Materials, Thomas Young Centre, Imperial College London, Exhibition Road, London SW7 2AZ, UK — ²Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, Düsseldorf 40237, Germany

As a binary end-member of many of the technologically highly interesting MAX phases, as well a useful refractory material in its own right, there is much to be gained from achieving a more accurate first-principles assessment of the behaviour of ZrC at ultra-high temperatures. Exploiting recent developments in finite-temperature density functional theory (DFT) calculations, we provide valuable data at temperatures where the available experimental data is of low accuracy. Within the framework of the UP-TILD approach [Grabowski 2007], the thermal expansion and heat-capacity of ZrC are calculated up to the melting-point. These fully anharmonic results are compared to calculations performed within the widely used quasi-harmonic approximation (QHA), which treats anharmonic effects in only an approximate manner. Sizeable deviations are found close to the melting point, consistent with the strongly anharmonic lattice vibrations present at such temperatures.

SYME 2.7 Tue 12:15 MA 004

Quo vadis electronic friction? Assessing vibrational lifetimes beyond the independent atom approximation — ●SIMON P. RITTMAYER¹, J. IÑAKI JUARISTI², JÖRG MEYER³, and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²Depto. & Centro de Física de Materiales (CSIC-UPV/EHU), San Sebastián, Spain — ³Leiden University, Leiden, The Netherlands

The quest for a both accurate and numerically efficient first-principles-based treatment of electronically non-adiabatic adsorbate dynamics on metal surfaces is still ongoing. A promising candidate in this regard is the concept of electronic friction within the local density friction approximation (LDFA). The numerical efficiency of this approach stems from an intrinsic decomposition and mapping of the interacting system to independent atoms individually embedded in a free electron gas. This inherent simplicity has raised serious conceptual concerns about the accuracy of this theory. On the other hand, it is not clear how much these approximations actually affect the description of “real” observables. In this regard, vibrational lifetimes of high-frequency adsorbate modes on metal surfaces provide a sensitive measure to gauge a non-adiabatic theory. We thus target this observable applying the LDFA for several well-studied systems and discuss it by comparing the results to other theoretical approaches as well as experimental data. Moreover, we present a simple and computationally efficient strategy to extend the LDFA beyond the yet indispensable frozen-surface and independent-atom approximation.

SYME 2.8 Tue 12:30 MA 004

Polynomial-oriented linear least squares fits of potential energy surfaces for quantum dynamics — ●FLORIAN HABECKER and THORSTEN KLÜNER — Universität Oldenburg, Germany

The field TD-QM Molecular Dynamics is facing two major problems within the BO-approximation: I. Solution of the TISE for the electrons and II. Solution of the TDSE for the nuclei. Electronic structure calculations result in a K-dimensional PES (K: number of d.f. for the nuclei) on which the motion of the nuclei is simulated, subsequently.

For economical reasons, the number of sampling points calculated by QC methods is generally smaller than those needed in the QD calculation. Hence, an interface is required to link the two major tasks. Taking the scalar energies E with the corresponding geometry parameters as input, the output of such an interface is a function to calculate any points of the PES, i.e. interpolated and extrapolated values.

Following classical papers on H₃⁺ [1 and refs. therein], the linear model function was chosen as a K-dimensional polynomial in this study. The lack of flexibility in this uniform ansatz was restored using appropriate non-linear variable transformations. Applying the method of LLS, precise fits can be calculated in a single non-iterative step. The

capability of this approach was validated with a set of 7942 ab initio data points from a 3-D PES of a CO/Ti₉O₁₈Mg₇¹⁴⁺-system [2]. Precise fits with chemical accuracy and better have been obtained for moderate expansions of the model function.

[1] W. Meyer, P. Botschwina, P. Burton, *J. Chem. Phys.* **84**, 891 (1986).

[2] H. Spieker, T. Klüner, *Phys. Chem. Chem. Phys.* **16**, 18743 (2014).

SYME 2.9 Tue 12:45 MA 004

Representing Complex Potential Energy Surfaces by Artificial Neural Networks — ●CHRISTOPHER HANDLEY and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Computer simulations of large systems are computationally costly, and in many cases intractable, when using ab initio methods. More efficient potentials are typically based on approximations specific for particular atomic interactions, and the fitting of these potentials is not straightforward. Neural Networks (NNs) can provide interatomic potentials that are comparable to the accuracy of quantum mechanical calculations [1,2]. They are flexible enough to fit complex functions to quantum mechanical training data and yield accurate energies and forces. Here, we present our recent work towards more transferable NN potentials. [1] C. M. Handley and P. L. A. Poplier, *J. Phys. Chem. A*, **114**, 3371–3383, (2010). [2] J. Behler, *PCCP*, **13**, 17901–18232 (2011).

SYME 2.10 Tue 13:00 MA 004

Kinetic Monte Carlo simulations of thin film growth with anisotropic particles — ●MIRIAM KLOPOTEK, MARTIN OETTEL, and FRANK SCHREIBER — Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

Thin film growth is a topic of fundamental experimental research, in particular for organic molecules with semiconducting properties. Thin films of organic molecules are composed of multiple ‘imperfect’ layers of the molecules, and the structures formed are of fundamental interest for various applications. Organic molecules are mostly highly anisotropic, rendering complex ordering at various length- and time-scales within the growing film that is not seen in the case of isotropic molecular/atomistic films [1]. We explore how this particle anisotropy affects the growth dynamics by means of computer simulations. We

have developed a novel algorithm to simulate large-scale thin film growth with rod-like particles using an accelerated Monte Carlo technique called *kinetic Monte Carlo* [2]. We discuss the simulations and the most relevant findings arising from statistical observables related to the orientational order of the rods. To relate the non-equilibrium growth structures to equilibrium we performed equilibrium calculations of a single layer of rods, as well. [1] S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, L. Cavalcanti, and O. Konovalov. Real-time observation of structural and orientational transitions during growth of organic thin films. *Phys. Rev. Lett.*, **96**:125504, March 2006. [2] Andrea C. Levi and Miroslav Kotrla. Theory and simulation of crystal growth. *Journal of Physics: Condensed Matter*, **9**(2):299, 1997.

SYME 2.11 Tue 13:15 MA 004

Ti and N adatom diffusion on, and N₂ desorption from TiN(001) surfaces via ab initio and classical molecular dynamics — ●DAVIDE G. SANGIOVANNI¹, DANIEL EDSTRÖM¹, LARS HULTMAN¹, IVAN PETROV^{1,2}, VALERIU CHIRITA¹, and JOE E. GREENE^{1,2} — ¹Thin Film Physics, IFM, Linköping University, Sweden — ²University of Illinois, Urbana-Champaign, Illinois, USA

We use classical and *ab initio* molecular dynamics to investigate fundamental atomistic processes and surface properties responsible for TiN surface evolution during thin film growth. The rate of adatom migration and N₂ desorption events are determined as a function of temperature to extract activation energies, attempt frequencies, and diffusion coefficients. Ti adatoms (Ti_{ad}), highly mobile on TiN(001) terraces, diffuse among fourfold hollow sites, primarily along <100> channels via single and long jumps. Ti_{ad} jumps on TiN(001) are highly correlated; an effect which leads to smaller diffusion coefficients than those determined via adatom random walks. Due to strong bonds formed with underlying N surface (N_{surf}) atoms, N adatoms (N_{ad}) are considerably less mobile on TiN(001) than Ti adatoms. After several N_{ad}/N_{surf}-pair exchange reactions, with very few N_{ad} jumps among neighboring stable surface sites, the N_{ad}/N_{surf} pair desorbs, leaving an anion surface vacancy which acts, in turn, as a catalyst for N₂ dissociative chemisorption. This pathway for N₂ desorption from TiN(001) is considerably more probable than N adatom recombination, which is kinetically hindered due to short-range N_{ad}/N_{ad} repulsive interactions.

SYME 3: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale II

Time: Tuesday 14:00–15:45

Location: MA 004

Invited Talk SYME 3.1 Tue 14:00 MA 004

First-principles theories of electron-plasmon and electron-spin fluctuation interactions in nanomaterials — ●JOHANNES LISCHNER — Imperial College, London, United Kingdom

The GW method includes an accurate treatment of many-electron interaction effects beyond density-functional theory and is the state-of-the-art approach for computing spectral functions and quasiparticle energies in nanomaterials. These quantities are measured in photoemission and tunneling experiments. Despite its great success, the GW approach has certain shortcomings and I will discuss two topics that require going beyond GW: i) plasmon satellites in spectral functions and ii) the coupling of quasiparticles to spin fluctuations.

Plasmon satellites in recent photoemission experiments on doped graphene have been interpreted in terms of novel plasmaron excitations, strongly coupled plasmon-hole states, predicted by GW theory. Using a cumulant expansion of the Green’s function to include higher-order electron-electron interaction effects and an accurate description of the substrate, I will demonstrate that no plasmaron states need to be invoked to explain the experiments. Similar conclusions are drawn for tunneling spectra of semiconductor quantum-well two-dimensional electron gases. I will also discuss the interaction of quasiparticles with spin fluctuations in iron selenide and demonstrate that significant coupling constants can give rise to superconducting transition temperatures consistent with experimental findings.

SYME 3.2 Tue 14:30 MA 004

Charge separation dynamics and opto-electronic properties of a diaminoterephthalate-C60 dyad — ●STEFANO PITTTALIS¹, ALAIN DELGADO¹, JÖRG ROBIN², LENA FREIMUTH³, JENS CHRISTOFFERS³, CHRISTOPH LIENAU², and CARLO ANDREA ROZZI¹ — ¹Istituto Nanoscienze - CNR, Modena, Italy — ²Institut fuer Physik and Center

of Interface Science, Carl von Ossietzky Universität, Oldenburg, Germany — ³Institut fuer Chemie and Center of Interface Science, Carl von Ossietzky Universität, Oldenburg, Germany

A novel dyad composed of a diaminoterephthalate scaffold, covalently linked to a Fullerene derivative, is explored as a nanosized charge separation unit powered by solar energy. Its opto-electronic properties are studied and the charge separation rate is determined. Simulations of the coupled electronic and nuclear dynamics in the Ehrenfest approximation are carried out on a sub 100 fs time scale after photoexcitation in order to gain insights about the mechanisms driving the charge separation. In particular, the role of vibronic coupling and of the detailed morphology are highlighted.

SYME 3.3 Tue 14:45 MA 004

Transferring spin into an extended π-orbital of a large molecule – ab-initio study of Au-PTCDA: Au(111) — ●T. DEILMANN¹, T. ESAT², B. LECHTENBERG³, P. KRÜGER¹, C. WAGNER², R. TEMIROV², F.B. ANDERS³, F.S. TAUTZ², and M. RÖHLFING¹ — ¹Institut für Festkörpertheorie, Universität Münster, Germany — ²Peter Grünberg Institute (PGI-3), FZ Jülich, Germany — ³Lehrstuhl für Theoretische Physik II, TU Dortmund, Germany

The combination of an organic molecule with an unpaired spin offers a large variety of interplay between spins and orbitals, with high sensitivity to structural and environmental details. Recently, a single Au atom on a PTCDA monolayer physisorbed on Au(111) has been investigated experimentally; it exhibits a Kondo peak in the STS spectrum.

In this talk we discuss ab-initio mean-field electronic spectra (which will then serve as input data for a subsequent NRG calculation to describe the Kondo effect). Based on ab-initio structural data (in agreement with observed STM images) we evaluate the electronic spectra by many-body perturbation theory within the *GW* approximation, as

well as, a simplified LDA+*GdW* approach [1]. For gas-phase PTCDA and Au-PTCDA, both methods agree well with one another and with available measurements. For Au-PTCDA on Au(111), a full *GW* calculation is too expensive due to the substrate. LDA+*GdW*, on the other hand, fully allows to incorporate the substrate polarizability in the self energy inside the molecule and leads to good agreement with the experimental data.

[1] M. Rohlfing, *Phys. Rev. B* **82**, 205127 (2010).

SYME 3.4 Tue 15:00 MA 004

Quasi-particle band structure of the transition-metal-based zero-gap semiconductors — ●MURAT TAS¹, ERSOY SASIOGLU², IOSIF GALANAKIS³, CHRISTOPH FRIEDRICH², and STEFAN BLÜGEL² — ¹Department of Basic Sciences, İstanbul Kemerburgaz University, 34217 İstanbul, Turkey — ²Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — ³Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece

Zero-gap semiconductors (SCs) are promising materials for a variety of applications ranging from spintronics to thermoelectricity. Using the *GW* approximation within the framework of the FLAPW method, we study the quasi-particle band structure of a number of transition-metal-based zero-gap SCs XX'YZ, where X, X' and Y are the transition metal elements, and Z is an *sp* element. We find that, in contrast to *sp*-electron based SCs such as Si and GaAs, the many-body renormalization has a minimal effect on the electronic band structure of these systems. It turns out that for many compounds the change of the band gap is less than 0.2 eV, which makes the starting point PBE a good approximation for the description of the electronic properties of these materials. Furthermore, the band gap can be tuned either by the variation of the lattice parameter or by the substitution of the Z element.

SYME 3.5 Tue 15:15 MA 004

Keldysh nonequilibrium Green's function vs. Feshbach projection operator approach for plasmon-assisted photoemission — ●YAROSLAV PAVLYUKH, MICHAEL SCHÜLER, and JAMAL BERAKDAR — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

A unified theoretical treatment of the single and double electron emission is achieved by using the Feshbach projection method. In this formalism the final target's state fixes the projection operator which subsequently determines the effective Hamiltonian and the optical potential for emitted electrons. The method of non-equilibrium Green's functions is a complementary approach which also allows to treat such processes diagrammatically. We explicitly establish a correspondence between these two approaches and illustrate the diagrammatic technique by calculations of the two-electron emission from C₆₀ assisted by the excitation of plasmons.

SYME 3.6 Tue 15:30 MA 004

Inclusion of thermal lattice vibrations and spin fluctuations within transport calculations — ●SERGIY MANKOVSKY, KRISTINA CHADOVA, DIEMO KÖDDERITZSCH, SVITLANA POLESYA, and HUBERT EBERT — Dept. Chemie/Physikalische Chemie, Universität München, Butenandtstr. 5-13, D-81377 München, Deutschland

We present an approach for the calculation of response quantities, e.g. Gilbert damping and electrical conductivity, accounting for temperature induced effects of lattice vibrations and spin fluctuations. The approach is based on the alloy analogy model with thermal vibrations and spin fluctuations modeled by random atomic displacements or magnetic moments deviations, respectively. We discuss various models to deal with spin fluctuations, determining their impact on the temperature dependent behaviour of conductivity and Gilbert damping parameter. We demonstrate the non-additivity of the separate contributions to the conductivity. The results of the calculations are compared to experimental data demonstrating a rather good agreement for the systems under consideration.

SYME 4: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale III

Time: Wednesday 10:30–13:30

Location: MA 004

Invited Talk

SYME 4.1 Wed 10:30 MA 004

Transport and excitations in biased nano-junctions: DFT-based simulations — ●MADS BRANDBYGE — Dept. of Micro and Nanotechnology, DTU-Nanotech, and Center for Nanostructured Graphene (CNG) Technical University of Denmark, Build. 345 east, 2800 Kongens Lyngby, DENMARK

In nano-junctions the electronic current is forced through a bottleneck down to the single molecular or atomic level. The highly non-equilibrium electronic system in such junctions results in various excitations such as phonons or plasmons. The phonon interaction directly yield signals in the current which can be probed in current-voltage spectroscopy, while the plasmon interaction can result in light emission which seems to be related to the current fluctuations/noise at finite frequency. The low frequency shot noise can provide information about the elastic transport channels and underlying spin-dependent electronic structure of the junctions. We will discuss how theory based on non-equilibrium Greens functions in combination with density functional theory or beyond, can be compared to experimental results, and provide important insights into excitations, the underlying transport channels, and electronic structure of the junctions. The electronic current will not only excite phonons. Energy non-conserving current-induced forces may control the resulting heat flow and heat distribution in the junctions, and in some cases lead to a break-down of the harmonic approximation.

SYME 4.2 Wed 11:00 MA 004

Role of atomic multiplets in intermediate valence SmB₆ and PuB₆ systems — ●ALEXANDER B. SHICK¹, ALEXANDER I. LICHTENSTEIN², and MIKHAIL I. KATSNELSON³ — ¹Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic — ²Institute of Theoretical Physics, University of Hamburg, Hamburg, Germany — ³Radboud University Nijmegen, The Netherlands

The materials with strong electron correlations are important because of the fundamental properties, and the technological applications. Re-

cently, SmB₆ (as well as PuB₆) was proposed as 3D topological insulator [1]. The electronic structure calculations are performed combining the LDA with an exact diagonalization of the Anderson impurity model [2] for [Sm,Pu]B₆. For the Sm atom in SmB₆, intermediate valence ground state (GS) is found with the *f*-shell occupation $\langle n_{4f} \rangle = 5.6$. The GS is a singlet, and the first excited triplet state ~ 3 meV higher in the energy. The *f*-orbital density of states is in agreement with experimental PE spectra. SmB₆ is a narrow band insulator already in LDA, with the direct band gap of ~ 10 meV. The electron correlations increase the band gap which now becomes indirect. For the Pu atom in PuB₆, we also find intermediate valence ($\langle n_{5f} \rangle = 5.5$) singlet GS. The calculations illustrate that many-body effects are relevant to form the indirect band gap, and support the idea of "topological Kondo insulator" in SmB₆. [1] M. Dzero *et al.*, *Phys. Rev. Lett.* **104**, 106408 (2010); [2] A. B. Shick *et al.*, *Phys. Rev. B* **87**, 020505(R) (2013).

SYME 4.3 Wed 11:15 MA 004

Transition paths and cohesive energies in alpha-sexithiophene polymorphs — ●BERNHARD KLETT, CATERINA COCCHI, and CLAUDIA DRAXL — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Like many organic crystals, oligothiophenes display polymorphism. Different molecular orientations and stacking arrangements are known to influence electronic and transport properties. An in-depth theoretical understanding of the energetics in these systems is crucial to control their growth and fully exploit their potential. In fact, their outstanding opto-electronic features make oligothiophenes excellent candidates for a number of technological applications, ranging from thin-film transistors to photovoltaic cells. We investigate alpha-sexithiophene in view of the transition between the high-temperature (HT) and low-temperature (LT) phase. With the full-potential all-electron density-functional theory code exciting [1], we analyse the cohesive properties of the two polymorphs. Our results indicate HT as the most stable phase, in agreement with previous molecular-dynamics simulations [2]. We also explore a transition path between the two polymorphs,

suggesting different reaction coordinates. Our findings allow for estimating the energy barrier between the two phases, hence gaining insight into the microscopic mechanisms ruling polymorphism in organic crystals. [1] A. Gulans, et al., *J. Phys.: Condens. Matter* 26, 363202 (2014). [2] R. G. Della Valle, et al., *J. Phys. Chem. A*, 112, 6715 (2008).

SYME 4.4 Wed 11:30 MA 004

Importance of the reorganization energy barrier in computational design of porphyrin-based solar cells with cobalt-based redox mediators — ●KRISTIAN BARUËL ØRNSØ, ELVAR ÖRN JÓNSSON, JUAN MARIA GARCIA-LASTRA, KARSTEN WEDEL JACOBSEN, and KRISTIAN SOMMER THYGESEN — Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

The shift from iodide based redox mediators in dye sensitized solar cells towards octahedral cobalt complexes has lead to a significant increase in the efficiency. However, due to the nature of this type of complexes the driving force required for the regeneration of the dye is very high and this limits the achievable efficiency. Here we show that the large driving force is a direct consequence of the large reorganization energy of the dye regeneration reaction. The reorganization energies for charge transfer between a simple zinc porphyrin dye and two popular cobalt based redox mediators is calculated using ab-initio molecular dynamics with explicit solvent. These results are then combined with a Marcus based extrapolation scheme to obtain the reorganization energies of more than five thousand porphyrin based dyes. We propose a scheme for scoring the performance of the porphyrin dyes which is able to identify already known high-performance dyes in addition to a number of even better candidates. Our analysis shows that large internal reorganization energy of the Co-based redox mediators is a main bottleneck for achieving higher efficiencies.

SYME 4.5 Wed 11:45 MA 004

Ab initio Simulation of Optical Limiting: The Case of Metal-Free Phthalocyanine — ●CATERINA COCCHI^{1,2}, DEBORAH PREZZI², ALICE RUINI^{2,3}, ELISA MOLINARI^{2,3}, and CARLO ANDREA ROZZI² — ¹Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — ²Centro S3, CNR Istituto-Nanoscienze, Modena, Italy — ³Dipartimento di Scienze Fisiche, Informatiche, Matematiche, University of Modena and Reggio Emilia, Italy

Optical limiting (OL) is a nonlinear process that is relevant for an entire class of devices related to the protection of light-sensitive elements, including the human eye, from intense light sources. While extensively studied experimentally, an accurate theoretical investigation of this phenomenon is still missing. In the framework of time-dependent density-functional theory, we present a fully ab initio, non-perturbative description of OL properties of a metal-free phthalocyanine, a prototypical macrocyclic organic compound. By applying a broadband electric field of increasing intensity, we confirm that reverse saturable absorption is the leading mechanism for OL phenomena in this class of systems, and reveal that a number of dipole-forbidden excitations are populated by excited-state absorption at more intense external fields. The excellent agreement with the available experimental data supports our approach as an effective and powerful tool to describe and predict OL [1]. [1] C. Cocchi et al., *Phys. Rev. Lett.* 112, 198303 (2014).

SYME 4.6 Wed 12:00 MA 004

High-throughput Screening of Perovskite Oxides and Related Compounds for Light Harvesting Applications — ●IVANO E. CASTELLI¹, NICOLA MARZARI¹, KRISTIAN S. THYGESEN², and KARSTEN W. JACOBSEN² — ¹Theory and Simulation of Materials, and EPFL National Center for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, Lausanne, Switzerland — ²Center for Atomic-scale Materials Design, Technical University of Denmark, Kgs. Lyngby, Denmark

Solar energy harvesting in a photoelectrochemical (PEC) cell, where water is split into hydrogen and oxygen, is an attractive and renewable contribution to our global needs of increasing energy demand and storage. We explore the possibility of identifying novel photocatalysts for PECs with the use of high-throughput quantum mechanical simulations. We devise inexpensive approaches to calculate systematically the structural and electronic properties of 19000 cubic ABX₃ perovskites, obtained by combining 52 possible metals as A- or B-cations, together with oxygen, nitrogen, sulfur and fluorine as anions. Using the screening criteria of stability and bandgap, 20 promising materials have been identified for visible-light harvesting [1]. The problem

of corrosion has been addressed, determining the Pourbaix diagrams of the candidates through a combination of experimental and computational data [2]. We also suggest a handful of lower symmetry layered and rare-earth perovskites for further theoretical and experimental investigation. References: [1] I. E. Castelli et al., *Energy Environ. Sci.* 5, 9034 (2012). [2] I. E. Castelli et al., *Topics in Catalysis* 57, 265 (2014).

SYME 4.7 Wed 12:15 MA 004

Understanding and designing novel materials for energy — ●SILVANA BOTTI — Friedrich-Schiller-Universität Jena, Germany

I will present an overview of our most recent theoretical/computational developments and some examples of their application to calculate from first-principles the structural and electronic properties of materials for energy production, storage, and saving.

The systems we are interested in are varied, ranging from thin-films absorbers and transparent conductive oxides for solar cells, to thermoelectrics, light-weight materials for constructions, complex hydrides for on-board hydrogen storage.

Nowadays, ab initio approaches based on density functional theory ally accuracy and efficiency, which make them suitable for understanding the physics not only of simple bulk crystals, but also of nanostructures, crystals with defects, doped crystals, interfaces, alloys, etc. As a consequence, ab initio calculations are finally able to analyze the "real" samples measured in experiments, allowing accurate comparisons of both ground-state and excited-state properties.

Moreover, ab initio methods can be used together with structural prediction algorithms and evolutionary algorithms to solve the inverse problem, i.e. find the best material for a specific application, providing a precious guide for experimental search of novel materials.

SYME 4.8 Wed 12:30 MA 004

Accurate density-functional theory calculation of bulk properties of 65 elemental solids — ●SVEN LUBECK¹, ANDRIS GULANS^{1,2}, and CLAUDIA DRAXL¹ — ¹Humboldt-Universität zu Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Density-functional theory (DFT) is a common method for calculating various properties of molecules and solids. While a large part of errors in DFT calculations stems from approximations to the exchange-correlation functional, there are additional not well controlled errors introduced by numerical implementation of electronic structure codes. In this work, we present accurate benchmark calculations of equation of state for 65 non-magnetic elemental solids. The data have been obtained using the full-potential augmented-plane-waves (APW) code `exciting` [1]. High accuracy has been achieved by constructing a converged APW+lo basis set, which yields consistent bulk properties of considered solids for a range of augmentation sphere sizes. Using methodology suggested in Ref. [2], we compare our results to those obtained with WIEN2k [2] and find the average and maximum Δ -values of 0.3 meV/atom and 2.1 meV/atom, respectively.

[1] A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, *J. Phys.: Condens. Matter* 26, 363202 (2014).

[2] K. Lejaeghere, V. Van Speybroeck, G. Van Oost and S. Cottenier, *Critical Reviews in Solid State and Materials Sciences* 39, 1-24 (2014).

SYME 4.9 Wed 12:45 MA 004

Electronic phase transitions of bismuth under strain from relativistic self-consistent GW calculations — IRENE AGUILERA, ●CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We present quasiparticle self-consistent GW (QS_{GW}) calculations of semimetallic bulk Bi. We go beyond the conventional QS_{GW} method by including the spin-orbit coupling throughout the self-consistency cycle. This approach improves the description of the electron and the hole pockets considerably with respect to standard density functional theory (DFT), leading to excellent agreement with experiment. We employ this relativistic QS_{GW} approach to conduct a study of the semimetal-to-semiconductor and the trivial-to-topological transitions that Bi experiences under strain. While DFT predicts that an unphysically large strain is needed for such transitions, we show that the relativistic QS_{GW} description of the electronic structure moves the required strain into a regime that is likely to be realizable in experiment. We acknowledge financial support from the Alexander von Humboldt Foundation and from the Helmholtz Association through the Virtual

Institute for Topological Insulators (VITI).

SYME 4.10 Wed 13:00 MA 004

A GW algorithm of reduced complexity for organic crystals — ●SABER GUEDDIDA¹, DIETRICH FOERSTER¹, PETER KOVAL², and DANIEL SANCHEZ-PORTAL² — ¹Laboratoire Ondes et Matière d'Aquitaine, University of Bordeaux, France — ²Donostia International Physics Center, San Sebastian, Spain

Density functional theory (DFT) provides a variational estimate of the electronic structure and geometry of many materials in their ground state. By its construction, DFT is unsuited for a description of the excited states, and particularly so for semi conductors. For these, one resorts to Hedin's GW approximation that gives rather good bands and gaps. A practical limitation of this approach is its computational cost that increases with the fourth power (N^4) of the number of atoms N per unit cell. Starting in 2007 [1], we have developed methods of "reduced complexity" that lower the growth of CPU time in calculations of electronic structure from N^4 to N^3 , both for optical absorption [2] and in the GW approximation for finite systems [3]. Here we report on the extension of our methods to crystals, where we reduce the growth of CPU time again from N^4 to N^3 , with N now the number of atoms in the unit cell of the crystal. Our work is motivated by organic semiconductors that have too many atoms in their unit cell for $O(N^4)$ algorithms to be practical. Our results should help to improve and optimize organic solar cells. [1] D. Foerster, J. Chem. Phys. 128 (34108) 2008. [2] P. Koval, D. Foerster and O. Coulaud, J. Chem. Theory Comp. 6 (2654) 2010. [3] D. Foerster, P.

Koval, and D. Sánchez-Portal, J. Chem. Phys. 135, 74105 (2011).

SYME 4.11 Wed 13:15 MA 004

Modeling anisotropic organic molecules at patterned semiconductor surfaces — ●NICOLA KLEPPMANN and SABINE H. L. KLAPP — Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Hybrid systems consisting of organic molecules at inorganic semiconductor surfaces are gaining increasing importance as thin film devices for optoelectronics. Their large charge carrier densities and tuneable resonance energies make them ideal candidates for semiconductor devices. However, the efficiency of such devices strongly depends on the self-organized structure formed by the adsorbed molecules, which depends, in turn, on the complex interplay of growth conditions and molecular properties. Recent ab initio calculations and experiments inspire us to examine the growth of sexiphenyl (6P) on ZnO(10-10) as a model system to understand self-organization of highly anisotropic molecules [1]. We develop a coarse-grained interaction hamiltonian of 6P molecules using a Gay-Berne potential and a linear quadrupole interaction term with additional substrate influence. We perform both equilibrium and non-equilibrium (growth) Monte Carlo simulations on a 2D lattice, where the rotational degrees of freedom of the molecules are continuous. We use these simulations to investigate orientational ordering in the condensed state, which is characterized by local descriptors such as order parameters and angular distributions.

[1] N. Kleppmann, and S. H. L. Klapp, submitted to JCP

[2] S. Bommel, N. Kleppmann et al., Nat Comm 5, 5388 (2014)

SYME 5: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale IV

Time: Wednesday 15:00–18:30

Location: MA 004

Invited Talk SYME 5.1 Wed 15:00 MA 004

Ultrafast coherent dynamics in photovoltaics — ●CARLO ANDREA ROZZI¹, SARAH MARIA FALKE², DANIELE BRIDA^{3,4}, MARGHERITA MAIURI⁴, MICHELE AMATO⁵, EPHRAIM SOMMER², ANTONIETTA DE SIO², ANGEL RUBIO^{6,7}, GIULIO CERULLO⁴, ELISA MOLINARI^{1,8}, and CHRISTOPH LIENAU² — ¹CNR-NANO, Modena, Italy — ²Carl von Ossietzky Universität, Oldenburg, Germany — ³University of Konstanz, Germany — ⁴CNR-IFN, Politecnico di Milano, Italy — ⁵Université Paris-Sud, Orsay, France — ⁶Universidad del País Vasco San Sebastián, Spain — ⁷Fritz-Haber-Institut, Berlin, Germany — ⁸Università di Modena e Reggio Emilia, Modena, Italy

The photoinduced charge-separation events occurring in photovoltaic systems have traditionally been interpreted in terms of the incoherent kinetics of optical excitations and of charge hopping, but recently signatures of quantum coherence were observed in energy transfer in photosynthetic bacteria and algae. We have studied charge separation in reference systems for artificial photosynthesis and photovoltaics by combining TDDFT simulations of the quantum dynamics and high time resolution femtosecond spectroscopy. We provide evidence that the coherent coupling between electronic and nuclear degrees of freedom is of key importance in triggering charge delocalization and transfer both in covalently bonded molecules and in bulk heterojunctions[1]. We have exploited the results of our research to design, synthesize and characterize a novel molecular scaffold for photovoltaic applications.[2] [1] Falke S., et al., Science, 344, 1001 (2014) [2] Pittalis S., et al., Adv. Func. Mat. (2014)

SYME 5.2 Wed 15:30 MA 004

Real-time propagation of coupled Maxwell-Kohn-Sham systems — ●RENE JESTÄDT¹, HEIKO APPEL^{1,3}, and ANGEL RUBIO^{1,2,3} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain — ³Max-Planck-Institut für Struktur und Materie, Hamburg

Based on a recent extension of time-dependent density-functional theory to quantum electrodynamics [1], we show first steps of an implementation of Maxwell's equations coupled to time-dependent Kohn-Sham equations. Our implementation utilizes the Riemann-Silberstein vector of the electromagnetic field which allows to write Maxwell's equations in a symplectic spinor representation similar to the Dirac equation. This spinor representation allows us to use standard unitary propagation techniques [2] developed for the Schrödinger equation

also for the coupled solution of Maxwell's equations and Kohn-Sham equations. We illustrate our implementation of such coupled Maxwell-Kohn-Sham systems in the real-space real-time code octopus [3] for small molecules coupled to optical cavities [4].

[1] M. Ruggenthaler et al., Phys. Rev. A **90**, 012508 (2014).

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

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

[4] M.S. Tame et al., Nature Physics 9, 329-340 (2013).

SYME 5.3 Wed 15:45 MA 004

Correlated Light-Matter Interactions in Cavity QED — ●JOHANNES FLICK¹, CAMILLA PELLEGRINI², MICHAEL RUGGENTHALER³, HEIKO APPEL^{1,4}, ILYA V. TOKATLY^{1,5}, and ANGEL RUBIO^{1,2,4} — ¹Fritz-Haber-Institut der MPG, Berlin — ²Nano-bio Spectroscopy Group/ETSF Scientific Development Centre, Universidad del País Vasco UPV/EHU, San Sebastian — ³Universität Innsbruck — ⁴MPI for the Structure and Dynamics of Matter, Hamburg — ⁵IKERBASQUE, Basque Foundation for Science, Bilbao

In the last decade, time-dependent density functional theory (TDDFT) has been successfully applied to a large variety of problems, such as calculations of absorption spectra, excitation energies, or dynamics in strong laser fields. Recently, we have generalized TDDFT to also describe electron-photon systems (QED-TDDFT) [1, 2]. Here, matter and light are treated on an equal quantized footing.

In this work, we present the first numerical calculations in the framework of QED-TDDFT. We show exact solutions for fully quantized prototype systems consisting of atoms or molecules placed in optical high-Q cavities and coupled to quantized electromagnetic modes. We focus on the electron-photon xc-contribution by calculating exact Kohn-Sham potentials using fixed-point inversions and present the performance of the first approximated xc-potential based on an optimized effective potential (OEP) approach.

[1] I. Tokatly, Phys. Rev. Lett. **110**, 233001 (2013).

[2] M. Ruggenthaler et al., Phys. Rev. A **90**, 012508 (2014).

SYME 5.4 Wed 16:00 MA 004

A hybrid QM/EMT approach to charge state corrections — ●OSMAN BARIS MALCIOGLU¹ and MICHEL BOCKSTEDTE² — ¹Lst.f.Theor.Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — ²FB Materialwissenschaften & Physik Universität Salzburg, 5020 Salzburg, Austria

Localized charge at surfaces, interfaces, or in volume materials natu-

rally occur due to the ionization of adsorbates or defects. A robust quantitative description of charged systems is a prerequisite to explore the physics of adsorbates, surface and bulk defects of materials such as metal oxides. The popular supercell approach requires charge neutrality per supercell. For charged systems this is enforced by compensation charges. The resulting spurious interaction can be corrected a-posteriori [1,2]. Recently, a scheme based on model fitting the localized charge and dielectric screening was proposed [1]. Here, we present a fully automated and efficient hybrid QM/EMT approach for handling long-reach fields. The response of the medium and the localized charge density of the ab-initio calculations are represented by a finite element function space. The relevant physical observables are obtained using an auto-adaptive mesh solver. We demonstrate applications of our approach to charge state corrections of surface and bulk defects slabs in comparison with the earlier approaches [1,2].

¹ H.-P. Komsa and A. Pasquarello, Phys. Rev. Lett. **110**, 095505 (2013).

² C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 016402 (2009).

SYME 5.5 Wed 16:15 MA 004

Plasmon assisted double photoemission — ●MICHAEL SCHÜLER, YAROSLAV PAVLYUKH, and JAMAL BERAKDAR — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

Coincidence measurements of double photoemission (DPE) represent a direct way of tracing the various facets of electronic correlations in molecular as well as extended systems, such as e. g. dynamical screening and collective excitations. One prominent example in this respect is the C_{60} molecule, for its plasmon resonances dominate the electronic excitation spectrum. Motivated by recent experiments on this molecule we demonstrate how the phenomenon of plasmon-mediated DPE can be described by an effective four-level system coupled to the bosonic plasmon excitations. The model generalizes the classical s -model and is treated within the GW approximation with the parameter estimates from *ab initio* calculations. We solve the coupled fermionic-bosonic time-dependent Kadanoff-Baym equations governing the dynamics of the model triggered by the interaction with the laser field. The use of the generalized Kadanoff-Baym Ansatz allows to significantly reduce the computation cost of our method.

SYME 5.6 Wed 16:30 MA 004

Calculating photoemission spectra with real-time density-functional theory — ●MATTHIAS DAUTH and STEPHAN KÜMMEL — University of Bayreuth, Germany

Photoemission spectroscopy is one of the primary tools for characterizing molecules and solids. A traditional approach of predicting photoemission signals relies on the interpretation of single-particle eigenvalues, e.g., from Hartree-Fock or Density Functional Theory (DFT). Here we demonstrate that real-time DFT allows for going beyond this static picture. We calculate photoemission signals dynamically and estimate ionization cross sections. We first investigate gas phase spectra, in which an ensemble of molecules with random orientation is probed. However, our approach in particular also allows for calculating angular resolved signals, i.e., we can track the ejected electron distribution with respect to a fixed light polarization. Furthermore, no a priori assumptions about the final state of the outgoing electrons need to be made, but the final state emerges naturally from the calculation. Thus, real-time DFT emerges as a powerful tool for the dynamical first-principles prediction of photoemission processes.

SYME 5.7 Wed 16:45 MA 004

Ab initio local field effects for surface second harmonic generation — ●NICOLAS TANCOCNE-DEJEAN^{1,2} and VALÉRIE VÉNIARD^{1,2} — ¹Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS-CEA/DSM, F. 91128, Palaiseau, France — ²European Theoretical Spectroscopy Facility (ETSF), France

A comprehensive understanding of the nonlinear optical properties of solids is crucial to improve the design and the analysis of new optical devices. Among these processes, Second-Harmonic Generation (SHG) is probably one of the most studied and has become, through the years a very powerful-non-invasive technique to characterize materials, because of its particular sensitivity to the symmetry of a system. In materials where inversion symmetry is present, optical Second Harmonic Generation is forbidden within the dipole approximation. But at a surface or an interface between two such materials, the inversion symmetry is broken and SHG is allowed.

Crystal local fields are generated by the induced microscopic re-

sponse of the system to an external perturbation. As a consequence their effects will be particularly important close to discontinuities as interfaces or surfaces. Local fields are important for a good description of optical properties of materials, but their effects on surface SHG have never been studied.

We present here a new ab initio formalism that allows us to calculate the frequency-dependent surface second-order susceptibility $\chi^{(2)S}$ within TDDFT, where the local field effects are fully included and we have applied this formalism to Silicon surfaces.

SYME 5.8 Wed 17:00 MA 004

Mapping atomic orbitals in the transmission electron microscope: seeing defects in graphene — ●LORENZO PARDINI¹, STEFAN LÖFFLER^{2,3}, GIULIO BIDDAU¹, RALF HAMBACH⁴, UTE KAISER⁴, CLAUDIA DRAXL^{1,5}, and PETER SCHATTSCHEIDER^{2,3} — ¹Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — ²Institute of Solid State Physics, Vienna University of Technology, Austria — ³University Service Centre for Transmission Electron Microscopy, Vienna University of Technology, Austria — ⁴Central Facility for Electron Microscopy, University of Ulm, Germany — ⁵European Theoretical Spectroscopy Facility (ETSF)

The possibility of mapping atomic orbitals by using energy-filtered transmission electron microscopy (EFTEM) has been considered for a long time and was recently demonstrated from a theoretical point of view. With the example of graphene, we predict how this approach can be used to map orbitals of a particular character. To this purpose, we have investigated graphene in its pristine structure and with two different kinds of defects, namely an isolated vacancy and a substitutional nitrogen atom. We show that basically three different kinds of images are to be expected, depending on the orbital character as determined from the corresponding projected density of states. To judge the feasibility of mapping such orbitals in a real microscope, we investigate the effect of the optics' aberrations, by simulating the lens system of two microscopes that are commonly used for electron energy loss spectrometry. We find that it should indeed be feasible to see atomic orbitals in a state-of-the-art EFTEM.

SYME 5.9 Wed 17:15 MA 004

Inelastic X-Ray Scattering: Insights from and Benefits for Many-Body Theory — ●CLAUDIA RÖDL, IGOR RESHETNYAK, FRANCESCO SOTTILE, and LUCIA REINING — Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau cedex, France

Non-resonant inelastic x-ray scattering (IXS) probes the momentum- and frequency-dependent dynamic structure factor $S(\mathbf{q}, \omega)$. It captures the neutral excitations of a many-body system, such as excitons, plasmons, and interband transitions. In particular, localized excitations that are forbidden in the optical limit of vanishing momentum transfer are accessible. $S(\mathbf{q}, \omega)$ is proportional to the diagonal element of the electric susceptibility $\chi(\mathbf{q}, \mathbf{q}', \omega)$. Thus, IXS directly probes the dielectric screening and, hence, the screened Coulomb interaction which governs, for instance, the formation of quasiparticles in photoemission spectroscopy and excitons in optical spectroscopy. Therefore, IXS provides a unique tool to disentangle the many-body physics of renormalized quasiparticles and neutral excitations. It may serve as a solid experimental reference for the development of new approaches in many-body theory. Moreover, the off-diagonal elements of $\chi(\mathbf{q}, \mathbf{q}', \omega)$ can be probed by coherent inelastic x-ray scattering (CIXS). This technique, which is still at a pioneering stage, allows one to visualize plasmon-like and localized neutral excitations in real space. We calculate diagonal and off-diagonal elements of $\chi(\mathbf{q}, \mathbf{q}', \omega)$ for semiconductors and transition-metal oxides in good agreement with experiment and discuss the rich physics that is contained in $\chi(\mathbf{q}, \mathbf{q}', \omega)$.

SYME 5.10 Wed 17:30 MA 004

Real-Space Multiple-Scattering X-ray Absorption Spectroscopy Calculations of d - and f -state Materials using a Hubbard Model — ●CHRISTIAN VORWERK¹, KEVIN JORISSEN¹, JOHN REHR¹, and TOWFIQ AHMED² — ¹Department of Physics, University of Washington, Seattle, Washington 98195 USA — ²Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 USA

We present calculations of the electronic structure and x-ray spectra of materials with correlated d - and f -electron states treated with the Hubbard model in a real-space multiple scattering (RSMS) formalism, and using a rotationally invariant local density approximation (LDA+ U). Values of the Hubbard parameter U are calculated ab initio

using the constrained random-phase approximation (cRPA). The real-space Green's function approach with Hubbard model corrections is an efficient way to describe localized electron states in strongly correlated systems, and their effect on core-level x-ray spectra. The method is shown to give the correct density of states and x-ray absorption spectra for Transition Metal- and Lanthanide-oxides such as Ce2O3 and NiO, where the traditional RSMS calculations fail.

Supported by DOE BES DE-FG02-97ER45623

SYME 5.11 Wed 17:45 MA 004

Variants of Second Order Screened Exchange for spin polarized and non-polarized Uniform Electron Gas — ●FELIX HUMMEL and GEORG KRESSE — University of Vienna, Austria

The commonly used Random Phase Approximation (RPA) only contains exchange processes of first order. The Second Order Screened Exchange (SOSEX) correction includes one exchange process beyond first order, which is considered the leading order correction to the RPA, and it has proven to be very accurate for the Uniform Electron Gas (UEG) as well as for solids.

The memory requirement of SOSEX is however of $O(N^4)$. We present an approach with a memory requirement of $O(N^2)$ and its differences to other approaches with comparable complexity, such as AC-SOSEX, for the spin polarized and non-polarized UEG.

SYME 5.12 Wed 18:00 MA 004

Ferromagnetism from strongly correlated electrons at the LaAlO₃/SrTiO₃ interface — ●FRANK LECHERMANN, LEWIN BOEHNKE, MALTE BEHRMANN, DANIEL GRIEGER, and CHRISTOPH PIEFKE — I. Institut für Theoretische Physik, Universität Hamburg

We shed light on the interplay between structure and many-body effects relevant for itinerant ferromagnetism in LaAlO₃/SrTiO₃ heterostructures. The realistic correlated electronic structure is studied by means of the (spin-polarized) charge self-consistent combination of density functional theory (DFT) with dynamical mean-field theory

(DMFT) beyond the realm of static correlation effects [1]. A ferromagnetic instability occurs only with oxygen vacancies and it is possible to account for the basic mechanism by an derived minimal Ti two-orbital e_g-t_{2g} description for the correlated subspace. Magnetic order affected by quantum fluctuations with a Ti moment of $0.2\mu_B$ builds up from effective double exchange, which can be traced to the dilute defect regime. [1] F. Lechermann, L. Boehnke, D. Grieger and C. Piefke, Phys. Rev. B 90, 085125 (2014)

SYME 5.13 Wed 18:15 MA 004

NanoDMFT: Full ab initio description of strong correlations in nanoscale devices — ●DAVID JACOB — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle

In order to obtain a full first-principles description of the correlated electronic structure and transport properties of nanoscale devices we combine the Coulomb-Hole-Screened-Exchange (COHSEX) approximation with Dynamical Mean-Field Theory (DMFT). While the former yields an effective mean-field description of the weakly correlated conduction electrons, the DMFT part accounts for the dynamic correlations originating e.g. from the strongly interacting $3d$ - or $4f$ -shells of transition metal atoms or from the molecular orbitals of weakly coupled molecular devices. The combination with COHSEX instead of Density Functional Theory (DFT) improves upon our NanoDMFT approach [1] in two important aspects: First, from the screened interaction W we can calculate the effective Coulomb interaction U for the strongly interacting electrons. Second, unlike in DFT+DMFT calculations the double-counting correction for COHSEX+DMFT is exactly known and straight-forward to calculate. Hence the two quantities which are essentially parameters in the DFT based approach can now be calculated ab initio so that it is now possible to actually predict e.g. the occurrence of the Kondo effect in magnetic atoms and molecules on metal surfaces and attached to metallic leads.

[1] D. Jacob *et al.*, PRL **103**, 016803 (2009); D. Jacob *et al.*, PRB **82**, 195115 (2010); M. Karolak *et al.*, PRL **107**, 146604 (2011); D. Jacob *et al.*, PRB **88**, 134417 (2013)

SYME 6: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale V

Time: Thursday 10:30–13:15

Location: MA 004

Invited Talk

SYME 6.1 Thu 10:30 MA 004

Interaction and Correlation Effects in Quasi Two-dimensional Materials — ●STEVEN G. LOUIE — Physics Department, University of California at Berkeley, and Lawrence Berkeley National Lab, Berkeley, CA 94720 USA

Experimental and theoretical studies of atomically thin quasi two-dimensional materials and their nanostructures have revealed that these systems can exhibit highly unusual behaviors. Owing to their reduced dimensionality, these systems present opportunities for manifestation of concepts/phenomena that may not be so prominent or have not been seen in bulk materials. Symmetry and many-body interaction effects often play a critical role in shaping qualitatively and quantitatively their properties. In this talk, we present some theoretical studies on graphene as well as other quasi-2D systems such as monolayer and few-layer transition metal dichalcogenides (e.g., MoS₂, MoSe₂, WS₂, and WSe₂) and metal monochalcogenides (such as GaSe and FeSe). Several quantum phenomena are discussed, including novel and dominant exciton effects, tunable magnetism, electron supercollimation by disorder, unusual plasmon behaviors, and possible enhanced superconductivity in some of these systems. We investigate their physical origins and compare theoretical predictions with experimental data.

SYME 6.2 Thu 11:00 MA 004

Screening of the Coulomb interaction in two-dimensional semiconductors: The case of transition metal dichalcogenides — ●ERSOY SASIOGLU, CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Experimentally determined large exciton binding energies and nonhydrogenic Rydberg series in monolayer transition metal (TM) dichalcogenides indicate a long-range behavior of the Coulomb interaction. By means of first-principles calculations in conjunction with the random-phase approximation [1,2] within the FLAPW method [3] we study screening of the Coulomb interaction in two-dimensional semiconduct-

ing TM dichalcogenides MX₂ (M=Cr, Mo, W; X=S, Se). We show that the screening in these systems deviates substantially from the bulk behavior, i.e., the short-range interaction is strongly screened, while the long-range interaction is anti-screened. This unconventional screening reduces the gradient of the Coulomb interaction giving rise to weak correlation effects, which explains the experimentally observed large exciton binding energies as well as the success of the one-particle density functional theory in the description of the electronic structure of these systems. This work has been supported in part by DFG-FOR-1346.

[1] C. Friedrich *et al.*, Phys. Rev. B. **81**, 125102 (2010).

[2] E. Şaşıoğlu *et al.*, Phys. Rev. B **83**, 121101(R) (2011).

[3] www.flapw.de

SYME 6.3 Thu 11:15 MA 004

Ultra-fast transient absorption spectra of monolayer MoS₂ by first principle — ●MARGHERITA MARSILI¹, DEBORAH PREZZI¹, DAVIDE SANGALLI², and ANDREA MARINI² — ¹CNR Istituto di Nanoscienze S3, Modena, Italy — ²CNR ISM, Montelibretti, Italy

We compute ultrafast transient absorption spectra of MoS₂ monolayers by employing a novel approach which combines density-functional and non-equilibrium Green's function theories. This approach allows the description of pump-probe optical experiments where the system is excited by an ultrashort laser pulse, and the variation of the optical response is probed at different time delays, thus providing a wealth of information on the fundamental physics of the relaxation processes. The case of monolayer MoS₂ is extremely challenging due to the interplay of excitonic, electron-phonon and spin-orbit coupling effects. We describe the excitation of the MoS₂ electronic system and follow the subsequent dynamics using a fully non-collinear spin formulation of the theory, including excitonic effects. The results are compared with experimental pump-probe data.

SYME 6.4 Thu 11:30 MA 004

Plasmon and exciton dispersion in two dimensions — ●PIER LUIGI CUDAZZO — LSI Ecole Polytechnique and ETSF, Palaiseau, France

Understanding the electronic properties of 2D materials requires the investigation of their elementary excitations that dictate their optical and transport properties. Using state-of-the-art Green's function many body approach we present a first principle study of the collective excitations (namely excitons and plasmons) in 2D materials. In particular from the evaluation of the dielectric function we investigated the exciton dispersion in graphane and hBN and the plasmon dispersion in metallic TMDs[1-3]. From our results we provide an exact analytic form of the two-dimensional screened potential. In contrast to 3D systems where the macroscopic screening can be described by a static dielectric constant in 2D systems the macroscopic screening is non local (q -dependent) showing a logarithmic divergence for small distances and reaching the unscreened Coulomb potential for large distances[4].

[1] P. Cudazzo, et. al. *New J. Phys.* 15 125005 (2013). [2] P. Cudazzo, et. al. (in preparation) [3] P. Cudazzo, et. al. *Phys. Rev. Lett.* 104 226804 (2010). [4] P. Cudazzo, et. al. *Phys. Rev. B* 84 085406 (2011).

SYME 6.5 Thu 11:45 MA 004

Origin of metallic edge states in transition-metal-dichalcogenide nanostructures — ●MARCO GIBERTINI and NICOLA MARZARI — Theory and Simulation of Materials (THEOS) and National Center for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, Switzerland

The existence of metallic edge states in transition-metal-dichalcogenide nanostructures has been reported both in the experimental and theoretical literature. Such nanostructures include for instance triangular islands and zigzag nanoribbons. Nonetheless, a thorough understanding of the mechanism giving rise to metallic states at the edge of such bulk insulating materials is still missing. Here we suggest a possible origin of such states and support our findings with first-principles density-functional-theory simulations. The key observation is that transition metal dichalcogenides like MoS_2 display a finite *formal* polarization that induces a charge reconstruction with the appearance of free carriers at the edges. We also suggest possible innovative applications in nanoelectronics and solar-energy devices.

SYME 6.6 Thu 12:00 MA 004

Starting-point dependence in the Bethe-Salpeter equation: example of rutile TiO_2 — ●OLGA TURKINA, UTE WERNER, DMITRII NABOK, and CLAUDIA DRAXL — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, D-12489 Berlin, Germany

Many-body perturbation theory, combining the GW approach and the Bethe-Salpeter equation (BSE), is a powerful tool for the description of one- and two-particle excitations. However, employing density functional theory as a starting point for these methods may lead to results that depend on the choice of the exchange-correlation (xc) functional. This starting-point dependence is well known for the G_0W_0 approximation. Such dependence is expected to occur also for BSE calculations, however, has not yet been investigated. With the example of rutile TiO_2 , we show that this is, indeed, the case. We employ two different xc functionals: the generalized gradient approximation (PBE) and a hybrid functional (PBE0'), combining a fraction of 25% exact exchange with PBE. The electronic structure is calculated using the G_0W_0 approximation. The BSE is solved to obtain the optical absorption spectra. These are analyzed with regard to the influence of eigenvalues, wave functions, and screening as originating from different xc functionals.

SYME 6.7 Thu 12:15 MA 004

Efficient exchange-correlation kernels for the description of excitonic effects in solids — ●SANTIAGO RIGAMONTI^{1,4}, SILVANA BOTTI^{2,4}, VALÉRIE VENIARD^{3,4}, CLAUDIA DRAXL^{1,4}, LUCIA REINING^{3,4}, and FRANCESCO SOTTILE^{3,4} — ¹Physics Department, Humboldt-Universität zu Berlin, Germany — ²Friedrich-Schiller Universität Jena, Institut für Festkörpertheorie und -optik — ³Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France — ⁴European Theoretical Spectroscopy Facility (ETSF)

One of the major challenges for time-dependent density-functional theory is the accurate and efficient description of excitonic effects in solids,

captured by the exchange-correlation (xc) kernel. In a recent empirical approach, the so-called "bootstrap" kernel has been proposed. Due to its high efficiency and some promising results [1] it appeared indeed interesting. In this work, we find a physically motivated derivation for it, opening the way to understand its weaknesses and to propose a new xc kernel. Our kernel is both simpler and more reliable, as confirmed by our numerical results [2]. We also propose a simple method to estimate exciton binding energies from the dielectric functions computed in the random-phase approximation alone. This method makes the approach accessible to a wide range of scientists.

[1] S. Sharma, J. K. Dewhurst, A. Sanna, and E. K. U. Gross, *Phys. Rev. Lett.* **107**, 186401 (2011).

[2] S. Rigamonti, S. Botti, V. Veniard, C. Draxl, L. Reining, and F. Sottile, *submitted*.

SYME 6.8 Thu 12:30 MA 004

Excitonic effects in many-body calculations — ●MATTEO GATTI^{1,2}, IGOR RESHETNYAK¹, GIORGIA FUGALLO¹, PIERLUIGI CUDAZZO¹, FRANCESCO SOTTILE¹, and LUCIA REINING¹ — ¹LSI, CNRS-Ecole Polytechnique and ETSF, Palaiseau, France — ²Synchrotron Soleil, Gif-sur-Yvette, France

The Bethe-Salpeter equation (BSE) is the state-of-art approach to calculate the absorption spectra of a large variety of materials [1]. Here we show that that the BSE is a powerful and accurate method also for the calculation of the exciton dispersion [2-4] (i.e. the exciton energy as a function of the momentum q carried by the electron-hole pair), and of the off-diagonal elements of the dielectric function in reciprocal space $\epsilon_{G,G'}(q, \omega)$ [5]. On the one hand, this allows the ab initio simulation of spectra measured by Electron Energy-Loss Spectroscopy (EELS) and Inelastic X-ray Scattering (IXS), including its Coherent version (CIXS), well beyond the optical limit $q \rightarrow 0$. On the other hand, this opens the door to the calculation of spectral functions [6-8] using the cumulant expansion for the Green's function G with a screened Coulomb interaction W that includes excitonic effects beyond the random-phase approximation employed in the GW approximation.

[1] G. Onida, et al., *Rev. Mod. Phys.* **74**, 601 (2002). [2] M. Gatti and F. Sottile, *Phys. Rev. B* **88**, 155113 (2013). [3] P. Cudazzo, et al., *Phys. Rev. B* **88**, 195152 (2013). [4] G. Fugallo, et al., unpublished. [5] I. Reshetnyak, et al., unpublished. [6] M. Guzzo, et al., *Phys. Rev. Lett.* **107**, 166401 (2011). [7] M. Gatti and M. Guzzo, *Phys. Rev. B* **87**, 155147 (2013). [8] M. Guzzo, et al., *Phys. Rev. B* **89**, 085425 (2014).

SYME 6.9 Thu 12:45 MA 004

Efficient parameter-free calculation of absorption spectra for insulators, semiconductors and metals from time-dependent current DFT — ●ARJAN BERGER — LCPQ - IRSAMC, Université de Toulouse III - Paul Sabatier, CNRS, Toulouse, France and European Theoretical Spectroscopy Facility

In this work we show that with a simple dynamical kernel we can obtain good absorption spectra from time-dependent current-density functional theory (TDCDFT) for insulators, semiconductors and metals. Our approach is fully parameter free since no artificial broadening parameter is used to match calculated and measured spectra. The cost of a calculation is equal to an RPA calculation. Moreover, our TD-CDFT approach scales better with system size than standard TDDFT implementations.

SYME 6.10 Thu 13:00 MA 004

Optical excitations in MoS_2 within ab-initio many-body perturbation theory — ●MATTHIAS DRÜPPEL, PETER KRÜGER, and MICHAEL ROHLFING — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, 48149 Münster, Germany

The transition metal dichalcogenides (TMDC), and MoS_2 as its most prominent member, open the door to a field of two dimensional atomically thin semiconductors which offer rich physics.

The state of the art theoretical description of electronic excitations in these materials starts with density-functional calculations (DFT), followed by the GW method in combination with a solution of the Bethe-Salpeter equation. The *converged* calculation (especially with respect to the size of the basis, i.e. number of plane waves, and k -meshes) of the last two steps has shown to be numerically extremely challenging.

We apply the efficient LDA+ GdW [1] approach to the excited states which enables us to describe electronic excitations in MoS_2 at substantially lower numerical cost. In the LDA+ GdW approximation the quasiparticle self-energy corrections to the LDA-DFT energies result

from the difference between the correct screening (semiconducting) and hypothetical metallic screening.

This approach sets us in a position where more atoms per unit cells

can be treated, e.g., for defects and for MoS₂ on substrates.

[1] M. Rohlfing, Phys. Rev. B. **82**, 205127 (2010)

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

SYME 7: Frontiers of Electronic Structure Theory: Many-Body Effects on the Nano-Scale VI

Time: Thursday 15:00–18:30

Location: MA 004

Invited Talk SYME 7.1 Thu 15:00 MA 004

Natural orbital functional theory with higher-order occupation probabilities — ●RALPH GEBAUER¹, ROBERTO CAR², and MORREL COHEN^{2,3} — ¹International Centre for Theoretical Physics (ICTP), Trieste, Italy — ²Department of Chemistry, Princeton University, Princeton, USA — ³Department of Physics and Astronomy, Rutgers University, USA

We introduce a novel energy functional for ground-state electronic-structure calculations. Its fundamental variables are the natural spin-orbitals of the implied singlet many-body wave function and their joint occupation probabilities. The functional derives from a sequence of controlled approximations to the two-particle density matrix. Algebraic scaling of computational cost with electron number is obtainable in general, and Hartree-Fock scaling in the seniority-zero version of the theory. Results obtained with the latter version for saturated small molecular systems are compared with those of highly-accurate quantum-chemical computations. The numerical results are variational, capturing most of the correlation energy from equilibrium to dissociation. Their accuracy is considerably greater than that obtainable with current density-functional theory approximations and with current functionals of the one-particle density matrix only.

SYME 7.2 Thu 15:30 MA 004

Electronic Properties of Surfaces and Interfaces with Self-Consistent Interatomic van der Waals Density Functional — ●NICOLA FERRI¹, ROBERT A. DISTASIO JR.², ALBERTO AMBROSETTI¹, ROBERTO CAR², MATTHIAS SCHEFFLER¹, and ALEXANDRE TKATCHENKO¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Princeton University, USA

Ubiquitous long-range van der Waals (vdW) interactions play a fundamental role in the structure and stability of a wide range of systems. Within the DFT framework, the vdW energy represents a crucial, but tiny part (0.001%) of the total energy, hence its influence on the electronic density, $n(\mathbf{r})$, and derived electronic properties is typically assumed to be rather small. Here, we address this question via a fully self-consistent (SC) implementation of the interatomic Tkatchenko-Scheffler vdW functional [1] and its extension to surfaces [2]. For several transition metal surfaces, self-consistency increases their dipole moments and induces non-trivial electron density rearrangements. As a consequence, we observed changes of up to 0.3 eV in the surface work-functions, with vdW self-consistency improving the agreement with experiments. Similar behavior is observed for molecules adsorbed on metals, where vdW contributions influence both Pauli push-back and charge transfer, the two phenomena that determine interface work-functions. [1] A. Tkatchenko and M. Scheffler, PRL (2009). [2] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, PRL (2012).

SYME 7.3 Thu 15:45 MA 004

Exact functionals for a lattice model — ●TANJA DIMITROV¹, HEIKO APPEL^{1,3}, and ANGEL RUBIO^{1,2,3} — ¹Fritz-Haber-Institut der MPG, Berlin — ²Nano-bio Spectroscopy Group/ETSF Scientific Development Centre, Universidad del País Vasco UPV/EHU, San Sebastian — ³MPI for the Structure and Dynamics of Matter, Hamburg

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, to gain insight into the behavior of the exact functional, and to devise new approximations, we investigate the exact solution of the many-body Schrödinger equation in Fock space for a lattice model with a softened Coulomb interaction term. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the *exact* density-to-potential and density-to-wave-function map. We discuss the behavior of functionals in the low-density limit.

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

SYME 7.4 Thu 16:00 MA 004

Many-body dispersion meets non-local density functionals: A unified approach for van der Waals correlations — ●JAN HERMANN, MATTHIAS SCHEFFLER, and ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

It is an ongoing challenge to develop an efficient method for van der Waals (vdW) non-local correlation within DFT which would be both accurate and broadly applicable. Current approaches can be loosely divided into the fragment-based ones, two-point density functionals and methods based on the density-density response function. The fragment-based models utilize parameters not derivable from the electron density. Two-point approaches are explicit density functionals, but difficult to generalize to include many-body correlations.

Here, we show that these seemingly contrasting approaches can be unified within a single framework based on the adiabatic-connection formalism in the random-phase approximation. We use a local response-function model from the VV09 functional [1] together with the many-body dispersion approach to create an atom-based model with no external parameters. We introduce a consistent correlation-functional-based coupling of the short- and long-range correlation energy. We show that this unification provides new insights into the different approaches, naturally deals with the partitioning of ionic and delocalized states and paves path towards self-consistent description of many-body vdW correlations.

[1] O. A. Vydrov, T. Van Voorhis, Phys. Rev. Lett. **103**, 063004

SYME 7.5 Thu 16:15 MA 004

Reduced Density-Matrix Functional Theory: correlation and spectroscopy — STEFANO DI SABATINO¹, JAN A. BERGER², LUCIA REINING³, and ●PINA ROMANIELLO¹ — ¹Laboratoire de Physique Théorique, CNRS, IRSAMC, Université Toulouse III - Paul Sabatier, Toulouse, France and ETSF — ²Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université Toulouse III - Paul Sabatier, CNRS, Toulouse, France and ETSF — ³Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, Palaiseau, France and ETSF

We study the performance of approximations to electron correlation in reduced density-matrix functional theory (RDMFT) and of approximations to the observables calculated within this theory [1]. We use the exactly solvable Hubbard molecule as test case. In particular we focus on the atomic limit and we explore how degeneracies and spin-symmetry breaking are treated in RDMFT. We find that, within the used approximations, RDMFT is not able to describe the signature of strong correlation in the spin-singlet ground state, whereas it give the exact result for the spin-symmetry broken case. [1] S. Di Sabatino, J.A. Berger, L. Reining, and P. Romaniello, submitted

SYME 7.6 Thu 16:30 MA 004

Does GW obey the straight-line condition? — MATTHIAS DAUTH^{1,3}, FABIO CARUSO², STEPHAN KUEMMEL¹, and ●PATRICK RINKE³ — ¹University of Bayreuth, Germany — ²University of Oxford, England — ³Aalto University, Helsinki, Finland

Many-body theory in the GW approach has become the method of choice for calculating charged excitations in solids. Recently, it is also increasingly being applied to molecules, but fundamental questions regarding its accuracy remain. One such fundamental theorem requires that the total energy changes linearly with gradual (i.e. fractional) ionisation of the molecule. In this work we investigate, if GW is piecewise linear or if it exhibits a derivation of the straight line error (DSLE). Since the derivative of the total energy with respect to the electron number gives the ionisation energy, we quantify the DSLE by taking the difference between the energy of the highest occupied state of the neutral and the lowest unoccupied state of the singly ionised molecule (which would be equal in the DSLE-free case). We find for a subset of molecules from the quantum chemical G2 benchmark set, that the DSLE in self-consistent GW amounts to 1.1 eV on average. This

DSLE can be mitigated in perturbative G_0W_0 by varying the starting point. We use density-functional theory as starting point and vary the amount of exact exchange α in the Perdew-Burke-Ernzerhof hybrid functional (PBEh). G_0W_0 becomes DSLE-free for $\alpha \approx 0.4$. The average deviation from the experimental IPs is then very close to that of self-consistent GW and amounts to ~ 0.25 eV.

SYME 7.7 Thu 16:45 MA 004

Green's Function embedding for Advanced Electronic Structure Methods based on Dynamical Mean-Field Theory — ●Wael Chibani¹, Xinguo Ren², Matthias Scheffler¹, and Patrick Rinke³ — ¹Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany — ²Key Laboratory of Quantum Information, USTC, Hefei, China — ³Aalto University, Helsinki, Finland

We introduce an embedding scheme for periodic systems that facilitates a self-consistent treatment of the physically important part of a system with electronic structure methods, that are computationally too expensive for periodic systems. We use dynamical mean-field theory [1] (DMFT) to couple to the rest of the system, which is treated with less demanding approaches such as Kohn-Sham density functional theory. In contrast to the original DMFT formulation for correlated model Hamiltonians, we consider here the unit cell as local 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 and GW self-energies (sc GW) for simple bulk systems. 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. For non self-consistent GW calculations we observe Plasmon satellites for Si – in good agreement with periodic G_0W_0 calculations [2] – that vanish at self-consistency. Our sc GW gap of ~ 0.9 eV for a two atom unit cell agrees well with previous G_0W_0 calculations and experiment. [1] A. Georges *et al.*, Rev.Mod.Phys.(2006), [2] M.Guzzo *et al.*, PRL(2011)

SYME 7.8 Thu 17:00 MA 004

Improved Ground State Electronic Structure and Optical Dielectric Constants With a Semi-Local Exchange Functional — ●Vojtěch Vlček¹, Gerd Steinle-Neumann¹, Linn Leppert¹, Rickard Armiesto², and Stephan Kümmel¹ — ¹University of Bayreuth, Germany — ²Linköping University, Sweden

For a set of solids, we explore a recently developed generalized gradient exchange functional (AK13) that has two characteristic features: its enhancement factor diverges for large reduced density gradients s as $s \ln(s)$ and its potential changes discontinuously at integer electron numbers. We apply the functional to semiconductors, Mott insulators, and ionic crystals and compare results for band structure and dielectric constants with a standard GGA. The AK13 functional provides a better description of the KS orbitals and we observe a qualitative improvement both in the bandgaps and in the optical dielectric constants, especially for the small gap semiconductors we explore (Ge, α -Sn, and CdO)

SYME 7.9 Thu 17:15 MA 004

Accurate, efficient localized resolution of identity of the Coulomb operator across the periodic table — ●Arvid Ihrig¹, Jürgens Wierferink¹, Igor Ying Zhang¹, Patrick Rinke^{1,2}, Volker Blum^{1,3}, and Matthias Scheffler¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Aalto University, Helsinki, Finland — ³Duke University, Durham, USA

A key component of advanced electronic structure methods is the explicit evaluation of the Coulomb operator. The corresponding four-center integrals can be solved with a “resolution of identity” (RI) approach for numeric atom-centered orbitals, as they are used in, e.g., FHI-aims [1]. In RI, basis function products are expanded in an auxiliary basis. The complete auxiliary basis is used for “RI-V”, the most accurate and most commonly used RI. We developed a localized RI (“RI-LVL”), which expands the products only in the subset of those auxiliary functions centered on the same atoms as the basis functions. This approach yields a superior scaling with system size, both in terms of computational time and memory requirements. At the same time it also retains the accuracy of the RI-V, as we have shown for HF, MP2, PBE0 and RPA calculations. The systems we investigated include weakly interacting molecular dimers (S22 test set) as well as TiO₂, Cu, and Au clusters. In all test cases we found that RI-LVL reproduces RI-V very accurately. Even for RPA-calculations of gold with very large basis sets the deviation to RI-V is only ~ 1.5 meV per atom. [1] V. Blum *et al.*, Comput. Phys. Commun. **180**, 2175 (2009).

SYME 7.10 Thu 17:30 MA 004

Explicitly correlated self consistent field theory — ●Christian Lasar and Thorsten Klüner — Carl von Ossietzky Universität, Oldenburg, Germany

There is a variety of methods available which aim to describe molecules and molecular reactions with chemical accuracy. The two main classes of these methods are density functional theory (DFT) and electron correlation approaches. DFT achieves great accuracy for many molecules and is applicable to quite large molecules. Unfortunately, DFT is not systematically improvable since the exact form of the exchange correlation functional remains unknown. Correlation methods do not suffer from this lack of systematic improvement. Unfortunately, they often require too much computational resources for large molecules. Additionally, they show a very slow convergence with the size of the basis set. Explicitly correlated methods are known to be able to solve this convergence problem. In these methods, the wavefunction is augmented with a function f_{ij} which explicitly depends on two electronic coordinates. Combining the advantages of low computational resources and the ability for systematic improvement, one ends up in the following ansatz for the wavefunction $\Psi = (1 + \sum_{ij} f_{ij})\Phi$, where Φ is one Slater determinant. With this ansatz the long determinant expansion is avoided. Additionally, there will be a fast convergence with the basis set size. We currently investigate the derivation of the working equations and their implementation for different functions f_{ij} . Some results for small molecules have already been obtained and will be presented in this contribution.

SYME 7.11 Thu 17:45 MA 004

Comparison of two self-consistent GW schemes — ●Peter Koval¹, Dietrich Foerster², and Daniel Sanchez-Portal^{1,3} — ¹Donostia International Physics Center, San Sebastián, Spain — ²Laboratoire Ondes et Matière d'Aquitaine, Bordeaux, France — ³Material Physics Center, San Sebastián, Spain

GW approximation (GWA) as a competitor of DFT provides a better description of electronic structure in several respects. However, a GW calculation is more expensive than similar DFT calculation. This fact contributed to a wide usage of simpler calculations based on GWA (SEX, COSEX, plasmon-pole approximations etc.) This manifold of approximations hampers a non-biased evaluation of merits of GWA to describe the electronic correlations. We produced a rigorous GW implementation where the only approximation is the use of localized orbitals [1]. The usage of spectral functions allowed us to realize two self-consistent GW schemes: sc GW [2] and qs GW [3] in one code [4]. Furthermore, we used all-electron Gaussian basis sets that allows for a coherent comparison with quantum chemistry methods. We use coupled-cluster methods CCSD and CCSD(T) as reference and compare ionization potentials of 15 molecules. The calculations show trends in sc GW and qs GW and give hints on possible sources of discrepancies/directions towards improving GWA . [1] D. Foerster, P. Koval, D. Sánchez-Portal, *J. Chem. Phys.* **135**, 074105 (2011); [2] L. Hedin, *J. Phys. Cond. Mat.* **11**, R489 (1999); [3] S. V. Faleev, M. van Schilfgaarde, T. Kotani, *Phys. Rev. Lett.* **93**, 126406 (2004); [2] P. Koval, D. Foerster, D. Sánchez-Portal, *Phys. Rev. B* **89**, 155417 (2014).

SYME 7.12 Thu 18:00 MA 004

Quasiparticle Self-Consistent GW for Molecules — ●Ferdinand Kaplan^{1,2,3}, Michiel van Setten^{1,2,5}, Florian Weigend^{1,3}, and Ferdinand Evers^{1,2,3,4} — ¹Institute of Nanotechnology (INT) — ²Institute for Theoretical Condensed Matter Physics (TKM) — ³Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany — ⁴Universität Regensburg, D-93040 Regensburg, Germany — ⁵Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

One of the most used approaches for the computational study of nanoscale systems and molecules is the density functional theory (DFT). However, DFT calculations of single particle excitation spectra, e.g. ionization potentials, often suffer from method-inherent difficulties. To systematically improve the estimation of quasi-particle energies for molecular system, we have implemented the GW method. The approach represents a perturbative expansion of the many-body Green's function with respect to the screened Coulomb interaction, W .

On G_0W_0 level the GW -self energy is calculated with the Kohn-Sham Green's function of the underlying DFT. Hence, one finds a strong dependence of the excitation energies on the reference system, i.e. DFT functionals. To overcome this problem, we implemented a self-consistent cycle which takes into account the deviations of the

quasiparticle(qp)-wavefunctions from their Kohn-Sham parents.

We find that this procedure converges to a fixed point solution which is independent of the reference system. For the testset of molecules analyzed by us so far, the results for ionization-energy and electron-affinity improve upon G_0W_0 , when comparing to experimental data.

SYME 7.13 Thu 18:15 MA 004

Pure state N-representability conditions: Should they be taken into account in Reduced density matrix functional theory? — •IRIS THEOPHILOU¹, NEKTARIOS LATHIOTAKIS^{2,3}, and NICOLE HELBIG¹ — ¹Peter Grünberg Institut (PGI-1), Forschungszentrum Jülich, Jülich, Germany — ²Theoretical and Physical Chemistry Institute (TPCI), National Hellenic Research Foundation, Athens,

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In Reduced Density Matrix Functional Theory (RDMFT) the natural occupation numbers are minimized under the ensemble N-representability conditions, i.e they are restricted to be between zero and one and sum to the number of electrons. Recently, the pure state N-representability problem for the one-body reduced density matrix has been solved [M. Altunbulak and A. Klyachko, Commun. Math. Phys. 282, 287 (2008)]. In this talk we discuss to which extend these pure state conditions are satisfied without being enforced in 3 electron systems using some standard RDMFT functionals. Our aim is to impose those pure state conditions that are not automatically satisfied and check whether this improves RDMFT results.