

TT 79: Frontiers of Electronic Structure Theory: Optical Excitation (organized by O)

Time: Wednesday 15:00–18:30

Location: MA 004

Invited Talk

TT 79.1 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)

TT 79.2 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).

TT 79.3 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 per-

formance 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).

TT 79.4 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 naturally 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).

TT 79.5 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 C₆₀ 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.

TT 79.6 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.

TT 79.7 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 response 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.

TT 79.8 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 SCHATTSCHNEIDER^{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.

TT 79.9 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 $\chi(\mathbf{q}, \mathbf{q}', \omega)$.

TT 79.10 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

TT 79.11 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.

TT 79.12 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)

TT 79.13 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 inter-

action 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)