

## CPP 31: Focused Session: Frontiers of Electronic Structure Theory - Non-equilibrium Phenomena at the Nano-scale IV (original: O, joined by CPP)

Time: Wednesday 10:30–13:15

Location: TRE Ma

**Topical Talk** CPP 31.1 Wed 10:30 TRE Ma  
**From Rydberg Crystals to Bound Magnons - Probing the Non-Equilibrium Dynamics of Ultracold Atoms in Optical Lattices** — ●IMMANUEL BLOCH — Max-Planck Institut für Quantenoptik, Garching, Germany — Ludwig-Maximilians-Universität, Munich, Germany

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

CPP 31.2 Wed 11:00 TRE Ma  
**Correlated Light-Matter Interactions in Cavity QED** — ●JOHANNES FLICK<sup>1</sup>, HEIKO APPEL<sup>1</sup>, and ANGEL RUBIO<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

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

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

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

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

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

CPP 31.3 Wed 11:15 TRE Ma  
**Optimized effective potential approach to time-dependent density functional theory for many-electron systems interacting with cavity photons** — ●CAMILLA PELLEGRINI<sup>1</sup>, JOHANNES FLICK<sup>2</sup>, HEIKO APPEL<sup>2</sup>, ILYA V. TOKATLY<sup>1,3</sup>, and ANGEL RUBIO<sup>1,2</sup> — <sup>1</sup>Nano-bio Spectroscopy Group and ETSF Scientific Development Centre, Departamento de Física de Materiales, Universidad del País Vasco UPV/EHU, E-20018 San Sebastián, Spain — <sup>2</sup>Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — <sup>3</sup>IKERBASQUE, Bilbao, Spain

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

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

CPP 31.4 Wed 11:30 TRE Ma  
**Correlated photon-electron wavefunctions in cavity Quantum Electrodynamics** — ●HEIKO APPEL<sup>1</sup>, JOHANNES FLICK<sup>1</sup>, RENE JESTAEDT<sup>1</sup>, and ANGEL RUBIO<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain

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

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

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

CPP 31.5 Wed 11:45 TRE Ma  
**Photoelectron driven plasmaron excitations in (2x2)K/Graphite** — ●BO HELLSING — Department of Physics, Gothenburg University, Sweden

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

CPP 31.6 Wed 12:00 TRE Ma  
**Charge-transfer excitations in organic systems from many-body perturbation theory** — ●XAVIER BLASE<sup>1</sup>, CARINA FABER<sup>1,2</sup>, PAUL BOULANGER<sup>1</sup>, CLAUDIO ATTACALITE<sup>1</sup>, and IVAN DUCHEMIN<sup>2</sup> — <sup>1</sup>Institut Néel, CNRS and UJF, Grenoble, France — <sup>2</sup>L.SIM/INAC, CEA, Grenoble, France

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

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

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

CPP 31.7 Wed 12:15 TRE Ma

**Charge transfer from first principles: self-consistent GW applied to donor-acceptor systems** — ●FABIO CARUSO<sup>1,2</sup>, VIKTOR ATALLA<sup>1</sup>, ANGEL RUBIO<sup>1,3</sup>, MATTHIAS SCHEFFLER<sup>1</sup>, and PATRICK RINKE<sup>1</sup> — <sup>1</sup>Fritz Haber Institute, Berlin, Germany — <sup>2</sup>University of Oxford, UK — <sup>3</sup>Universidad del País Vasco, San Sebastián, Spain

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

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

CPP 31.8 Wed 12:30 TRE Ma

**What Koopmans' compliant orbital-density dependent functionals can do for you: a comprehensive benchmark of the G2-set** — ●GIOVANNI BORCHI<sup>1</sup>, NGOC LINH NGUYEN<sup>1</sup>, ANDREA FERRETTI<sup>2</sup>, ISMAILA DABO<sup>3</sup>, and NICOLA MARZARI<sup>1</sup> — <sup>1</sup>École Polytechnique Fédérale de Lausanne, Lausanne (VD), CH — <sup>2</sup>Centro S3, CNR-NANO, Modena, IT — <sup>3</sup>Department of Materials Science and Engineering, Penn State University, University Park (PA), USA

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

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

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

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

CPP 31.9 Wed 12:45 TRE Ma

**The electronic structure of quinacridone: Optimally tuned range-separated hybrid functional versus GW results** — DANIEL LÜFTNER<sup>1</sup>, SIVAN REFAELY-ABRAMSON<sup>2</sup>, MICHAEL PACHLER<sup>1</sup>, MICHAEL G. RAMSEY<sup>1</sup>, LEEOR KRONIK<sup>2</sup>, and ●PETER PUSCHNIG<sup>1</sup> — <sup>1</sup>Institut für Physik, Karl-Franzens-Universität Graz, Austria — <sup>2</sup>Department of Materials and Interfaces, Weizmann Institute of Science, Israel

Quinacridone is an organic molecule (C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>) utilized in the formation of organic pigments. It has also been discussed for usage in organic electronics particularly due to its stability under ambient conditions and its tendency to form self-assembled supramolecular networks. Here, we report on its electronic structure, both, for the isolated molecule as well as for the alpha- and beta- bulk molecular crystal polymorphs. We employ an optimally tuned range-separated hybrid functional (OT-RSH) within density functional theory as well as GW corrections within a many-body perturbation theory framework. A comparison of the theoretical results obtained with the different levels of theory and a subsequent comparison with experimental data from angle-resolved photoemission spectroscopy emphasize the need for going beyond simple semi-local DFT-functionals in order to obtain the correct orbital ordering. Furthermore the comparison indicates that the results obtained with OT-RSH greatly improve those of standard DFT functionals and achieve an agreement with experiment at the level of GW calculations, thus making the OT-RSH an alternative to the computationally more expensive GW approach.

CPP 31.10 Wed 13:00 TRE Ma

**GW many-body perturbation theory for electron-phonon coupling calculations** — ●CARINA FABER<sup>1,2</sup>, PAUL BOULANGER<sup>1</sup>, IVAN DUCHEMIN<sup>1,2</sup>, and XAVIER BLASE<sup>1</sup> — <sup>1</sup>Institut Néel, CNRS, Grenoble, France — <sup>2</sup>INAC, CEA, Grenoble, France

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

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