

## CPP 67: Focus Session: Frontiers of Electronic-Structure Theory: Correlated Electron Materials VI (joint session O/MM/DS/TT/ CPP)

Organizers: Silke Biermann, Ecole Polytechnique, Palaiseau cedex, France; Paul R. Kent, Oak Ridge National Laboratory, USA; Matthias Scheffler, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin (Synopsis provided with part I of this session)

Time: Thursday 10:30–12:45

Location: HL 001

CPP 67.1 Thu 10:30 HL 001

**Core-level spectroscopy with the *GW* approximation** — ●DOROTHEA GOLZE and PATRICK RINKE — Department of Applied Physics, Aalto University, Espoo, Finland

Inner-shell spectroscopy is an important tool to characterize molecules, liquids and adsorption processes at surfaces. We present a new, accurate method for computing X-ray photoelectron spectra based on the *GW* approximation that overcomes the limitations of density functional theory based approaches. Green's function theory in the *GW* approximation has become the method of choice for addition and removal energies of valence electrons in solids and is now increasingly being applied to molecules. However, *GW* core-level spectroscopy has thus far not received any attention. In most *GW* implementations, the self-energy is computed in the imaginary frequency domain followed by an analytic continuation to the real frequency axis. However, our calculations show that the analytic continuation becomes highly inaccurate for frequencies far away from the Fermi level and is not suitable for the computation of core excitations. Thus, we evaluate the self-energy on the real-frequency axis using the contour deformation (CD) technique. We implemented CD in combination with a resolution-of-the-identity approximation for the screened Coulomb interaction in the FHI-aims program package. Test calculations reveal that our implementation reproduces Turbomole reference calculations [1] perfectly. Furthermore, we present benchmark studies of small and medium-sized gas-phase molecules and discuss the potential of our method for more complex systems. [1] M. J. van Setten et al. *JCTC*, 2013, 232

CPP 67.2 Thu 10:45 HL 001

***GW* and beyond from matrix resolvents** — ●JAN GESENHUES<sup>1</sup>, DMITRII NABOK<sup>2</sup>, MICHAEL ROHLFING<sup>1</sup>, and CLAUDIA DRAXL<sup>2</sup> — <sup>1</sup>Institut für Festkörpertheorie, Westfälische Wilhelms-Universität, 48149 Münster, Germany — <sup>2</sup>Theoretische Festkörperphysik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

Typically *GW* calculations make use of either plasmon pole models or numerical integration in order to determine the screened Coulomb interaction *W*. We demonstrate how to obtain an analytical representation of *W* with the help of a matrix resolvent and present some standard *GW* results which have been obtained with the method. The analytical *W* is a useful starting point for subsequent calculations involving vertex corrections. On the other hand, the matrix resolvent technique itself can be applied upon a BSE-like equation of motion for the polarizability to include vertex corrections.

CPP 67.3 Thu 11:00 HL 001

**Electron-Magnon Scattering in Elementary Ferromagnets from First Principles: Lifetime Broadening and Kinks** — MATHIAS C. T. D. MÜLLER, ●CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We study the electron-magnon scattering in bulk Fe, Co, and Ni within the framework of many-body perturbation theory implemented in the full-potential linearized augmented-plane-wave method. Starting from the *GW* approximation we obtain a Bethe-Salpeter equation for the two-particle (electron-hole) Green function, where single-particle Stoner excitations and collective spin-wave excitations (magnons) are treated on the same footing. We employ the solution of the Bethe-Salpeter equation to construct a self-energy that describes the scattering of electrons and magnons. The resulting renormalized electronic band structures exhibit strong spin-dependent lifetime effects close to the Fermi energy, which are strongest in Fe. In the case of Co and Ni, the renormalization gives rise to kinks in the electronic band dispersion at low binding energies, which we attribute to electron scattering with spatially extended spin waves. Furthermore, we find a band anomaly at larger binding energies in iron, which results from a coupling of the quasihole with single-particle excitations that form a peak in the Stoner continuum. This band anomaly has, in fact, been observed in

recent photoemission experiments at the same energy and momentum.

CPP 67.4 Thu 11:15 HL 001

**Effects of the Tamm-Dancoff approximation on the optical spectra of organic molecules** — ●TOBIAS LETTMANN and MICHAEL ROHLFING — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

When calculating excited state properties of electronic systems within the many-body perturbation theory (MBPT), the Bethe-Salpeter equation (BSE) needs to be solved. This is often done within the so called Tamm-Dancoff approximation (TDA), neglecting the coupling of resonant and anti-resonant excitations.

It is generally accepted that the TDA is justified for large, extended systems e.g. bulk crystals. However it has been shown that the TDA may no longer hold for some organic semiconductors<sup>1</sup>. In this talk we discuss the effects of the TDA on the resulting optical spectra of organic molecules of different sizes and investigate for which cases the TDA may still be justified.

<sup>1</sup> B. Baumeier et al: *J Chem. Theory Comput.*, 2012, 8, 997

CPP 67.5 Thu 11:30 HL 001

**Ab-initio treatment of non-local electronic correlations with the dynamical vertex approximation** — ●ANNA GALLER<sup>1</sup>, PATRIK THUNSTRÖM<sup>2</sup>, PATRIK GUNACKER<sup>3</sup>, JOSEF KAUFMANN<sup>3</sup>, MATTHIAS PICKEM<sup>3</sup>, JAN M. TOMCZAK<sup>3</sup>, and KARSTEN HELD<sup>3</sup> — <sup>1</sup>Centre de Physique Theorique, Ecole Polytechnique, 91128 Palaiseau, France — <sup>2</sup>Department of Physics and Astronomy, Materials Theory, Uppsala University, 75120 Uppsala, Sweden — <sup>3</sup>Institute of Solid State Physics, TU Wien, 1040 Vienna, Austria

Recently, approaches such as the dynamical vertex approximation (DΓA) or dual-fermion method have been developed. These diagrammatic approaches are going beyond dynamical mean-field theory (DMFT) by including non-local electronic correlations on all length scales as well as the local DMFT correlations. Here we present our efforts to extend the DΓA methodology to ab-initio materials calculations (AbinitioDΓA). Our approach is a unifying framework which includes both, *GW* and DMFT-type of diagrams, but also important non-local correlations beyond, e.g. non-local spin fluctuations. In our multi-band implementation we are using a worm sampling technique within continuous-time quantum Monte Carlo in the hybridization expansion to obtain the DMFT vertex, from which we construct the reducible vertex function in a ladder approximation. As a first application we show results for transition metal oxides. Support by the ERC project AbinitioDGA (306447) is acknowledged.

References: [1] A. Galler, P. Thunström, P. Gunacker, Jan M. Tomczak, and K. Held, *Physical Review B* 95, 115107 (2017)

CPP 67.6 Thu 11:45 HL 001

**Non-local correlations in effectively reduced spatial dimensions** — ●JAN M. TOMCZAK<sup>1</sup>, MATTHIAS PICKEM<sup>1</sup>, BENJAMIN KLEBEL<sup>1</sup>, ANNA GALLER<sup>2</sup>, JOSEF KAUFMANN<sup>1</sup>, PATRIK GUNACKER<sup>1</sup>, PATRIK THUNSTRÖM<sup>3</sup>, THOMAS SCHÄFER<sup>2</sup>, ALESSANDRO TOSCHI<sup>1</sup>, and KARSTEN HELD<sup>1</sup> — <sup>1</sup>Institute of Solid State Physics, TU Wien, Austria — <sup>2</sup>Centre de Physique Théorique, Ecole Polytechnique, Palaiseau, France — <sup>3</sup>Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden

Using the dynamical vertex approximation and its recent extension for electronic structure calculations, AbinitioDΓA[1], we explore the impact of spatial dimensions onto non-local correlations: (a) we compare magnitude and manifestations of non-local self-energies in ultra-thin films of transition-metal oxides to those in the bulk material. (b) we track the evolution of non-local correlations in the doped Hubbard model when continuously going from 3D to 2D. In particular we probe the limits of the “space-time separation” of electronic correlations evidenced in 3D[2]. Support by the ERC project AbinitioDGA (306447) and the Austrian Science Fund (FWF) projects I 2794-N35

and P 30213-N36 is acknowledged.

References: [1] A. Galler, P. Thunström, P. Gunacker, JMT, K. Held, PRB 95, 115107 (2017), [2] T. Schäfer, A. Toschi, JMT, PRB 91, 121107R (2015)

CPP 67.7 Thu 12:00 HL 001

**Does the optical signature of oxidized polyethylene stem from saturated or unsaturated carbonyl defects?** — ●GUIDO ROMA<sup>1</sup>, FABIEN BRUNEVAL<sup>1</sup>, and LAYLA MARTIN-SAMOS<sup>2</sup> — <sup>1</sup>DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, F-91191 Gif sur Yvette, France — <sup>2</sup>CNR-Demokritos, Trieste, Italy

Polyethylene (PE), one of the simplest and most used aliphatic polymers, is generally provided with a number of additives, in particular antioxidants, because of its tendency to get oxidized. Carbonyl defects, a product of the oxidation of PE, are occurring in various forms, in particular saturated ones, known as ketones, where a C=O double bond substitutes a CH<sub>2</sub> group, and various unsaturated ones, i.e., with further missing hydrogens. Many experimental investigations of the optical properties in the visible/UV range mainly attribute the photoluminescence of PE to one specific kind of unsaturated carbonyls, following analogies to the emission spectra of similar small molecules. However, the reason why saturated carbonyls should not be optically detected is not clear. We investigated the optical properties of PE with and without carbonyl defects using perturbative GW and the Bethe-Salpeter equation in order to take into account excitonic effects. We discuss the calculated excitonic states in comparison with experimental absorption/emission energies and the stability of both saturated and unsaturated carbonyl defects. We conclude that the unsaturated defects are indeed the best candidate for the luminescence of oxidized PE, and the reason is mainly due to oscillator strengths.

CPP 67.8 Thu 12:15 HL 001

**Bethe-Salpeter equation beyond the Tamm-Dancoff approximation at finite momentum transfer: Absorption and loss spectra including excitonic effects** — ●BENJAMIN AURICH, CATERINA COCCHI, and CLAUDIA DRAXL — Humboldt-University, Berlin, Germany

The state-of-the-art ab-initio method for computing optical properties of semiconductors is based on the Bethe-Salpeter equation (BSE) which describes the excitations of the system in terms of interacting electron-hole (e-h) pairs. For absorption spectra, typically no momentum transfer from light to the e-h pairs is considered, and the

coupling between excitations and de-excitations of e-h pairs is usually neglected by using the Tamm-Dancoff approximation (TDA). This approach yields excellent agreement with experiment for many materials, but may break down for confined systems [1]. The TDA is also known to fail to describe the electron energy loss spectra for materials as simple as silicon [2]. We report on the extensions of the open-source code exciting [3] allowing for BSE calculations beyond the TDA and at finite momentum transfer using an exact diagonalization scheme [4]. We demonstrate the differences between TDA and non-TDA spectra at vanishing and finite momentum transfer for periodic molecular systems.

[1] M. Grüning et al., Nano Lett **9**, 2820 (2009)

[2] V. Olevano and L. Reining, Phys. Rev. Lett. **86**, 5962 (2001)

[3] A. Gulans et al., J. Phys. Condens. Matter **26**, 363202 (2014)

[4] T. Sander et al., Phys. Rev. B **92**, 045209 (2015)

CPP 67.9 Thu 12:30 HL 001

**Calculations of charge and spin susceptibilities and quasiparticle energy shifts within the CASTEP plane-wave DFT code** — ●VINCENT SACKSTEDER<sup>1</sup>, EVGENY PLEKHANOV<sup>2</sup>, PHIL HASNIP<sup>3</sup>, MATT PROBERT<sup>3</sup>, STEWART CLARK<sup>4</sup>, KEITH REFSON<sup>1</sup>, and CEDRIC WEBER<sup>2</sup> — <sup>1</sup>Royal Holloway University of London, UK — <sup>2</sup>Kings College London, UK — <sup>3</sup>University of York, UK — <sup>4</sup>University of Durham, UK

CASTEP is a pseudopotential based plane wave code which scales to the largest supercomputers and offers a wide feature set. Within CASTEP we have implemented calculation of the charge and spin susceptibility tensor, which describes the response to a perturbing charge or spin. We present corrections to the Kohn-Sham energies obtained by using the susceptibility tensor to screen Hartree-Fock exchange. In the static limit this is the SEX part of the COHSEX approximation, and if instead the dynamic susceptibility is used one obtains the GW approximation.

Our memory and CPU consumption scales linearly with the plane wave basis size, allowing thorough exploration of convergence with basis size, not only of the susceptibility itself, but of the SEX and GW quasiparticle shifts. We emphasize that our calculations are heavily parallelized, in exactly the same way as a standard DFT ground state calculation.

This work will allow first principles calculations of magnon spectra, exchange couplings, ionization potentials, and KKR and DMI coefficients.