

## TT 65: Focused Session: Frontiers of Electronic Structure Theory 7 (jointly with HL and O)

Time: Thursday 16:00–19:00

Location: H36

TT 65.1 Thu 16:00 H36

**Determination of the one-body Green's function: freedom and constraints** — GIOVANNA LANI<sup>1,4</sup>, ●PINA ROMANIELLO<sup>2,4</sup>, and LUCIA REINING<sup>3,4</sup> — <sup>1</sup>Forschungszentrum Jülich, Jülich, Germany — <sup>2</sup>Laboratoire de Physique Théorique-IRSAMC, CNRS, Université Paul Sabatier, Toulouse, France — <sup>3</sup>Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DSM, Palaiseau, France — <sup>4</sup>European Theoretical Spectroscopy Facility (ETSF)

The one-particle Green's function  $G$  plays a key role in many-body physics due to the wealth of physical information that it contains. In this work we go beyond the standard methods to calculate  $G$ , which are plagued by various shortcomings, and we use an approximate set of functional differential equations relating the one-particle Green's function to its functional derivative with respect to an external perturbing potential [1]. We show that this set of equations has, in principle, multiple solutions, but that only one is well behaved - this is the physical solution. We give the formally exact family of solutions, which depends on an auxiliary quantity  $q$ , for which we find stringent exact constraints. Our findings suggest that once  $q$  is known, the physical solution is uniquely fixed by the vanishing Coulomb interaction limit [2-3].

[1] L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics (W.A. Benjamin Inc., New York, 1964)

[2] G. Lani, P. Romaniello, and L. Reining, New Journal of Physics, 14, 013056 (2012)

[3] G. Lani, P. Romaniello, and L. Reining, in preparation

TT 65.2 Thu 16:15 H36

**Restoring piecewise linearity in density-functional theory** — ●ISMAILA DABO<sup>1</sup>, ANDREA FERRETTI<sup>2</sup>, MATTEO COCCIONI<sup>3</sup>, and NICOLA MARZARI<sup>4</sup> — <sup>1</sup>Ecole des Ponts ParisTech, Marne-la-Vallée, France — <sup>2</sup>CNR-Istituto Nanoscienze, Modena, Italy — <sup>3</sup>University of Minnesota, Minneapolis, USA — <sup>4</sup>EPFL, Lausanne, USA

Electronic-structure calculations based upon density-functional theory (DFT) have been fruitful in diverse areas of condensed matter physics. Despite their exceptional success, it can hardly be denied that a range of fundamental electronic properties fall beyond the scope of current DFT approximations. Many of the failures of DFT calculations take root in the lack of piecewise linearity of approximate functionals, which reverberates negatively on the electronic-structure description of systems involving fractionally occupied and spatially delocalized electronic states, including but not restricted to dissociated molecules, adsorbed species, charge-transfer complexes, and semiconducting compounds. In this talk, I will present a novel class of first-principles methods that restores the piecewise linearity of the total energy by imposing Koopmans' theorem to DFT approximations. The Koopmans-compliant approach is apt at describing full orbital spectra within a few tenths of an electron-volt relative to experimental direct and inverse photoemission data. This level of accuracy is comparable to the predictive performance of accurate many-body perturbation theory methods at a fraction of their computational cost, and with the additional benefit of providing accurate total energies for systems with fractional occupations.

TT 65.3 Thu 16:30 H36

**Self-interaction-corrected and Koopmans-compliant functionals: from molecules to solids** — ●GIOVANNI BORGHI<sup>1</sup>, LINH NGUYEN<sup>1</sup>, ANDREA FERRETTI<sup>2</sup>, ISMAILA DABO<sup>3</sup>, and NICOLA MARZARI<sup>1</sup> — <sup>1</sup>Theory and Simulation of Materials, EPFL, Lausanne — <sup>2</sup>CNRNANO, University of Modena and Reggio Emilia — <sup>3</sup>Ecole des Ponts ParisTech, Université Paris-Est

We present an overview of the performance of self-interaction corrected, orbital-density dependent functionals as applied to the calculation of the electronic structure of atoms, molecules and solids.

In particular, we show how orbital-dependent corrections of Koopmans' compliant functionals are able to restore not only the correct ionization energies, but also the eigenvalues of low-lying single-particle states with an accuracy comparable or better to that of many-body perturbation theory, while retaining a variational principle which grants the possibility to optimize geometries and bond lengths.

The outcome of these orbital-density dependent calculation remain, even in the thermodynamic limit, Wannier-like orbitals, that localize

thanks to a condition related to the Edmiston-Ruedenberg criterion. These localized functions can be used as Wannier interpolators of band structures, allowing to discuss the performance of the functionals in the solid-state limit.

TT 65.4 Thu 16:45 H36

**Lattice density functional theory at finite temperature with strongly density-dependent exchange-correlation potentials** — ●STEFAN KURTH<sup>1</sup>, GAO XIANLONG<sup>2</sup>, A-HAI CHEN<sup>2</sup>, and ILYA TOKATLY<sup>1</sup> — <sup>1</sup>Univ. of the Basque Country UPV/EHU, San Sebastian, Spain and IKERBASQUE, Basque Foundation for Science, Bilbao, Spain — <sup>2</sup>Zhejiang University, Jinhua, China

The derivative discontinuity of the exchange-correlation (xc) energy of density functional theory (DFT) at integer particle number is absent in many popular local and semilocal approximations. In lattice DFT, approximations exist which exhibit a discontinuity in the xc potential at half filling but due to convergence problems of the Kohn-Sham (KS) self-consistency cycle, the use of these functionals is mostly restricted to situations where the local density is away from half filling. Here a numerical scheme for the self-consistent solution of the lattice KS Hamiltonian with a local xc potential with rapid (or quasi-discontinuous) density dependence is suggested. The problem is formulated in terms of finite-temperature DFT where the discontinuity in the xc potential emerges naturally in the limit of zero temperature. A simple parametrization is suggested for the xc potential of the uniform 1D Hubbard model at finite temperature obtained from the thermodynamic Bethe ansatz. The feasibility of the numerical scheme is demonstrated by application to a model of fermionic atoms in a harmonic trap. The corresponding density profile exhibits a plateau of integer occupation at low temperatures which melts away for higher temperatures.

TT 65.5 Thu 17:00 H36

**Kohn-Sham equations beyond the single-determinant approximation** — NEKTARIOS N. LATHIOTAKIS<sup>1</sup>, ●NICOLE HELBIG<sup>2,3</sup>, NIKITAS I. GIDOPOULOS<sup>4</sup>, and ANGEL RUBIO<sup>3,5</sup> — <sup>1</sup>Theoretical and Physical Chemistry Institute, NHRF, Athens, Greece — <sup>2</sup>Peter-Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich, Jülich, Germany — <sup>3</sup>Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, CFM CSIC-UPV/EHU-MPC and DIPC, San Sebastián, Spain — <sup>4</sup>ISIS, STFC, Rutherford Appleton Laboratory, HSIC, Didcot, United Kingdom — <sup>5</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We describe a new method for the optimization of the total energy in reduced density matrix functional theory (RDMFT) which reduces the computational costs to the costs of a density functional calculation within the optimized effective potential method. Within this method the natural orbitals are restricted to be solutions of a single-particle Schrödinger equation with a local effective potential which in addition to reducing the computational costs also provides an energy eigenvalue spectrum connected to the natural orbitals. This energy spectrum is shown to reproduce the ionization potentials of different atoms and molecules very well. In addition, the dissociation limit is well described without the need to break any spin symmetry, i.e. this attractive feature of RDMFT is preserved.

TT 65.6 Thu 17:15 H36

**Initial stages of time-evolution of excitations in Fermi liquids and finite systems** — ●YAROSLAV PAVLYUKH<sup>1</sup>, JAMAL BERAKDAR<sup>1</sup>, and ANGEL RUBIO<sup>2</sup> — <sup>1</sup>Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — <sup>2</sup>Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre, Dpto. de Física de Materiales, Universidad del País Vasco, CFM CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain

A particle-hole excitation in a many-body system is not an eigenstate and, thus, evolves in time. The evolution at short times after an excitation with the energy  $\epsilon$  was created is the quadratic decay with the rate constant  $\sigma^2(\epsilon)$ . Later, after some set-in time  $\tau(\epsilon)$ , the exponential decay develops. It is governed by another rate constant  $\gamma(\epsilon)$ .

We study the electron-boson model for the homogenous electron gas and use the first order (in boson propagator) cumulant expansion of

the electron Green's function. In addition to a quadratic decay in time upon triggering the excitation, we identify non-analytic terms in the time expansion similar to those found in the Fermi edge singularity phenomenon.

Finite systems (J. Chem. Phys., **135**, 201103 (2011)) give an opportunity to test the conjectured behavior numerically as an exact solution of a many-body problem is feasible. We propose a simple model for the electron spectral function that links together all three aforementioned parameters and give a prescription how the energy uncertainty  $\sigma^2(\epsilon)$  can be computed within the many-body perturbation theory.

TT 65.7 Thu 17:30 H36

**Real-structure effects from *ab-initio* calculations** — ●ANDRE SCHLEIFE — Condensed Matter and Materials Division, Lawrence Livermore National Laboratory, Livermore, CA, USA

By harnessing the power of supercomputers, *computational materials science* is becoming a field that enables insight into fundamental materials physics. It is inevitable to further push *ab-initio* approaches, allowing them to account for effects that are important at the forefront of experimental research.

I will present the solution of the Bethe-Salpeter equation as a recent theoretical-spectroscopy technique and how it is extended and used to understand real-structure effects in oxide and nitride semiconductors. This talk will illustrate the success of our modification of this framework to describe the interplay of free electrons and excitonic effects in *n*-doped ZnO. Combining a cluster expansion scheme and electronic-structure calculations allows to explore the potential for band-gap tailoring in oxide and nitride alloys. These material systems are a driving force of current semiconductor technology, e.g. for solar cells and solid-state lighting; understanding fundamental effects will help to overcome performance limits.

In addition, computational materials science can *replace* dangerous experiments, e.g. in the context of radiation damage: I will present large-scale simulations of non-adiabatic electron-ion dynamics based on real-time time-dependent density functional theory that explain electronic stopping as an important mechanism responsible for radiation damage when fast H or He ions penetrate aluminum.

TT 65.8 Thu 17:45 H36

**Specwer: an efficient first-principle program for electronic structures and spectroscopic simulations of nanomaterials** — ●BIN GAO — Center for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

Although nanomaterials have been routinely synthesized and analyzed in various laboratories around the world, they still present great challenges for theoretical studies using the *ab initio* and/or first-principle methods due to the simple fact that they are too large to handle for the conventional theoretical approaches. Various linear-scaling methods have been proposed in recent decades to circumvent this difficulty. In this talk, I will present our recently developed program Specwer and its applications for electronic structures and spectroscopic simulations of different nanomaterials. For large-scale molecules, Specwer program employs the reduced single-electron density matrix and divide-and-conquer method. I will show its applications in the ground and excited states of nanomaterials at various density functional theory levels, in which the information of excited states is obtained via solving the so-called Liouville-von Neumann equation. I will also highlight the importance of including the spin-orbit coupling in some cases, for instance, the L-edge X-ray absorption spectroscopy, and the electron transport in double-stranded DNA molecules.

TT 65.9 Thu 18:00 H36

**Generalized incomplete-basis-set correction applied to EXX-OEP** — ●MARKUS BETZINGER, CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We recently derived [1] an incomplete-basis-set correction (IBC) for all-electron response functions within the full-potential linearized augmented plane-wave (FLAPW) method as realized in the FLEUR code [2]. The IBC utilizes the potential dependence of the LAPW basis functions whose response is calculated explicitly by solving radial Sternheimer equations in the spheres. While in the original formulation of the IBC [1] only spherical perturbations of the potential have been taken into account, we show here an extension to non-spherical perturbations, replacing the single radial Sternheimer equation for each angular momentum  $\ell$  by a set of equations coupling different angular

momenta. Likewise, the response of the core electrons is computed. We demonstrate that this generalized IBC improves further the convergence in terms of basis-set size and number of unoccupied states. We apply the generalized IBC to the exact-exchange (EXX) optimized-effective-potential (OEP) approach. While for simple semiconductors and insulators the original IBC already leads to a physical and stable local EXX potential, we show that for more complex materials like NiO, whose band gap is formed by *d* states, the generalization of the IBC is crucial to obtain a well-converged local optimized potential.

[1] M. Betzinger *et al.*, Phys. Rev. B **85**, 245124 (2012)

[2] <http://www.flapw.de>

TT 65.10 Thu 18:15 H36

**One particle spectral function and analytic continuation for many-body implementation in the exact muffin-tin orbitals method** — ●ANDREAS ÖSTLIN<sup>1</sup>, LIVIU CHIONCEL<sup>2,3</sup>, and LEVENTE VITOS<sup>1,4,5</sup> — <sup>1</sup>Department of Materials Science and Engineering, Applied Materials Physics, KTH Royal Institute of Technology, Stockholm SE-100 44, Sweden — <sup>2</sup>Augsburg Center for Innovative Technologies, University of Augsburg, D-86135 Augsburg, Germany — <sup>3</sup>Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany — <sup>4</sup>Department of Physics and Astronomy, Division of Materials Theory, Uppsala University, Box 516, SE-751210, Uppsala, Sweden — <sup>5</sup>Research Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Budapest H-1525, P.O. Box 49, Hungary

We investigate one of the most common analytic continuation techniques in condensed matter physics, namely the Padé approximant. Aspects concerning its implementation in the exact muffin-tin orbitals (EMTO) method are scrutinized with special regard towards making it stable and free of artificial defects. We discuss the difference between the **k**-integrated and **k**-resolved analytical continuations, as well as describing the use of random numbers and pole residues to analyze the approximant. It is found that the analytic properties of the approximant can be controlled by appropriate modifications. At the end, we propose a route to perform analytical continuation for the EMTO + dynamical mean field theory (DMFT) method.

TT 65.11 Thu 18:30 H36

**Core-electron forces within the FLAPW method** — ●DANIEL AARON KLÜPPELBERG, MARKUS BETZINGER, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany

The full-potential linearized augmented-plane-wave method (FLAPW) is an all-electron electronic-structure method based on density functional theory (DFT). Characteristic to the method is that space is divided into spheres around the atoms, so called 'muffin-tins', and an interstitial region in between. Local orbitals can be used to describe semicore states within the valence-state formalism. It is established as an accurate tool for describing many properties of complex materials.

We address the occurrence of contributions to the forces due to core electrons described by wave functions having tails exceeding the muffin-tin boundary. Accurate forces are needed not only for relaxing the atomic structure to its ground state, but also in order to calculate precise phonon spectra via the finite-displacement method. We present a core-tail correction to the Pulay force term found by Yu *et al.* [1], implemented into the FLEUR code [2], which deals with the core electrons. This addition extends the known formula over the whole unit cell and therefore includes the complete force contribution coming from core states that extend beyond their muffin-tin. In this talk, we will present examples on the performance of this addition in comparison to the inclusion of local orbitals and the adjustment of the muffin-tin radii.

[1] R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991)

[2] [www.flapw.de](http://www.flapw.de)

TT 65.12 Thu 18:45 H36

**The linearized augmented lattice-adapted plane wave basis** — ●GREGOR MICHALICEK and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The full-potential linearized augmented plane wave method (FLAPW) is an all-electron electronic structure method that provides density functional results for complex solids with very high precision, irrespective of the chemical element of the solid. For this purpose the Kohn-Sham wavefunctions are expanded into LAPW basis functions. These

are plane waves in an interstitial region (IR) that are augmented by atom-centered functions in non-overlapping spheres around each atom. The LAPW basis features many desirable properties that are a key component to the high precision of the FLAPW method.

In this talk we show that the capability of the FLAPW method can be kept with a modification of the basis-set that is numerically more efficient. We argue that the required plane-wave cut-off of the interstitial part of the LAPW basis results mostly from mathematical

conditions and the efficiency of the LAPW description can be increased by incorporating more physics into the construction of this part of the basis. We propose a linearized augmented lattice-adapted plane wave basis ((LA)<sup>2</sup>PW) that replaces the plane waves in the IR by smart linear combinations of plane waves, show how to realize an efficient implementation of such a basis, and provide a construction principle for the linear combination of plane waves. The so constructed basis is evaluated in terms of precision and calculation runtime performance.