

O 84: Focused session: Frontiers of electronic structure theory: Strong correlations from first principles VI (jointly with TT)

Time: Friday 10:30–13:00

Location: HE 101

Topical Talk O 84.1 Fri 10:30 HE 101
Dynamically screened Coulomb interaction and GW self-energy in transition metal compounds — ●TAKASHI MIYAKE — AIST, Tsukuba, Japan

We present a procedure for constructing low-energy models from first-principles using the GW-RPA and Wannier function technique. The procedure starts with dividing the Hilbert space into two subspaces: the low-energy part (d space) and the rest of the space (r space). The low-energy model is constructed for the d space by eliminating the degrees of freedom of the r space. The effective electron interaction of the model is expressed by a partially screened Coulomb interaction which is calculated in the constrained random-phase-approximation (cRPA), where screening channels within the d space are subtracted. As an illustration, the procedure is applied to 3d transition metals, 3d perovskite oxides, and iron-based superconductors. It is found that strength of electron correlation is strongly material dependent. Self-energy effects in quasiparticle bandstructure are analyzed using the GW approximation, which is the lowest-order expansion in the screened Coulomb interaction. Effects of dynamic screening and non-local self-energy (in the Wannier basis) are discussed.

O 84.2 Fri 11:00 HE 101

The Electronic Structure of CuO: Quasiparticles and Satellites — ●CLAUDIA RÖDL, FRANCESCO SOTTILE, and LUCIA REINING — Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau, France and European Theoretical Spectroscopy Facility (ETSF)

The insulating transition-metal oxide CuO is considered a key to understanding the electronic structure of high-temperature superconducting cuprates, since it features similar bonding geometries. The photoemission spectra of this oxide, which is usually termed to be strongly correlated, have not been explained satisfactorily by first-principles calculations up to now. Special difficulties arise from the close entanglement of the structural and electronic degrees of freedom in this compound, which is due to the unoccupied Cu *3d* orbitals.

In contrast to the local-density approximation of density-functional theory (DFT), which predicts CuO to be a metal, we obtain finite band gaps by means of hybrid functionals containing screened exchange and the DFT+*U* method. Starting from these qualitatively correct band structures, we perform many-body calculations in the GW approximation. The various approaches to the one-particle excitation spectra are compared to experimental results. We discuss whether or not the peaks occurring in the photoemission data are quasiparticle excitations or satellite structures, respectively.

O 84.3 Fri 11:15 HE 101

Ab-initio description of satellites in graphite — ●MATTEO GUZZO¹, LORENZO SPONZA¹, CHRISTINE GIORGETTI¹, FRANCESCO SOTTILE¹, DEBORA PIERUCCI², MATHIEU G. SILLY², FAUSTO SIROTTI², JOSHUA J. KAS³, JOHN J. REHR³, and LUCIA REINING¹ — ¹Ecole Polytechnique, Palaiseau, FR — ²Synchrotron SOLEIL, Gif-sur-Yvette, FR — ³U. Washington, Seattle, USA

The GW method has been very successful in describing photoemission spectra in a variety of systems. In particular, GW is known to give good quasiparticle properties like band-gaps, but it has shown some limitations in the description of complex correlation effects like satellites. Satellite peaks in photoemission come from higher-order excitations and are still poorly studied in the valence bands. In perturbative GW the spectral function can describe additional features beside the quasiparticle peaks, but these satellites are known to be too weak and too low in energy, as it appears from calculations on the Homogeneous Electron Gas and some real materials. We have recently shown that including additional diagrams in the Green's function (similarly to what has been done with the cumulant expansion) we obtain an excellent description of satellites series in the test case of bulk silicon [1], where GW is unable to cope. We now focus on a more complex system, i.e. graphite, with this same approach. Using our newly measured XPS valence data, we investigate the effects of anisotropies on satellites and give a prediction on the spectral changes following the transition towards a single graphene layer. **Refs:** [1] M. Guzzo *et al.*, Phys. Rev. Lett. 107, 166401 (2011)

O 84.4 Fri 11:30 HE 101

Internal elasticity of graphene-based systems — ●PASQUALE PAVONE^{1,2}, ROSTAM GOLESORKHTABAR^{1,2}, JÜRGEN SPITALER^{1,2}, and CLAUDIA AMBROSCH-DRAXL¹ — ¹Chair of Atomistic Modelling and Design of Materials, University of Leoben, Austria — ²Materials Center Leoben Forschung GmbH, Leoben, Austria

When a crystal undergoes a strain deformation, the lower symmetry of the deformed structure may allow for internal relaxations of atomic positions which do not follow the macroscopic applied strain. These relaxations can be described introducing the concept of internal-strain tensor [1], which relates the local deformation to the macroscopic strain. In this work, we present a first-principles calculation of the linear and non linear internal-strain tensors for a monolayer graphene as well as for hexagonal graphite. In order to analyze the relevance of the internal relaxation for hexagonal structures, results are also compared with *ab-initio* data for the cubic diamond phase. Calculations are performed using the pseudo-potential density-functional-theory code Quantum ESPRESSO [2] and both the local-density and generalized-gradient approximations for the exchange-correlation energy. The accuracy of the result of this investigation allows to solve some open issues arising in the literature from previous model [3] as well as *ab-initio* [4] calculations.

[1] C.S.G. Cousins, J. Phys.: Condens. Matter **14**, 5091 (2002)[2] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009)[3] C.S.G. Cousins and M.I. Heggie, Phys. Rev. B **67**, 024109 (2003)[4] R. Wang *et al.*, Physica B: Condens. Matter **405**, 3501 (2010)

O 84.5 Fri 11:45 HE 101

Accounting for dynamical screening in optical absorption spectra — ●LORENZO SPONZA^{1,2}, MATTEO GUZZO^{1,2}, CHRISTINE GIORGETTI^{1,2}, and LUCIA REINING^{1,2} — ¹LSI-Ecole Polytechnique, Palaiseau, France — ²ETSF : European Theoretical Spectroscopy Facility

In optics, absorption spectra are computed via the evaluation of the two particle correlation function *L* of the material which is given by the differentiation of the single particle Green's function *G*₁ with respect to an external (perturbing) potential *U*. State of the art calculations of optical absorption spectra rely on the Bethe-Salpeter Equation (BSE) and they make use of static screening *W*. Though, the inclusion of dynamical effects at a BSE level is a subject of both theoretical and technological interest. As an example, in some photovoltaic cells multiple-exciton generation (MEG)[2] has been proposed to improve drastically the efficiency of the device but to describe absorption in the presence of MEG one has to account for the dynamical screening.

Recently *G*₁ has been derived as exact solution of a differential functional equation which allows the explicit treatment of *W*(ω) [1]. Inspired by this work, we extended its strategy to the case of absorption, that is to the computation of *L*. We found a non-linear integro-differential equation that can be solved through some careful approximation. In this work we present an analysis of the solution of the problem and a comparison with standard Bethe-Salpeter approach.

[1] M.Guzzo *et al.*, Phys. Rev. Lett. **107**, 166401 (2011) [2] for MEG see for example Kheifets *et al.*, Phys. Rev. B **68**, 233205 (2003)

O 84.6 Fri 12:00 HE 101

Quasiparticle Spectra from Self-Consistent GW Calculations for Transition-Metal Monoxides — ●MERZUK KALTAK and GEORG KRESSE — Computational Materials Physics University of Vienna, Austria

We present calculations for the transition-metal monoxides MnO, FeO, CoO and NiO within the framework of many-body perturbation theory, specifically using a self-consistent GW approximation with vertex corrections. Using a maximally localized Wannier projection, the band structure seems to be predicted reasonably well in the antiferromagnetic phase AFII at *T* = 0. The stacking of ferromagnetic planes in the [111] direction causes a reduction of the symmetry, which consequently leads to a splitting of the *t*_{2g} bands into *a*_g and energetically more favourable *e*_g states. We show that scGW quasiparticle band gaps are closer to experiment than previously published results obtained from conventional *ab-initio* methods using a nonlocal exchange-correlation functional with a subsequent not self-consistent *G*₀*W*₀ calculation. In

addition to the electronic structure we investigate the optical properties of the compounds. To this end, the Bethe-Salpeter equation in the independent particle picture for the irreducible polarizability is solved and the optical spectrum $\epsilon(\omega)$ is calculated.

O 84.7 Fri 12:15 HE 101

Unified description of ground and excited states of finite systems: the self-consistent GW approach — ●FABIO CARUSO¹, PATRICK RINKE¹, XINGUO REN¹, ANGEL RUBIO^{1,2}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut, Berlin, Germany — ²Universidad del Pais Vasco, San Sebastian, Spain

Fully self-consistent GW calculations – based on the iterative solution of the Dyson equation – provide an approach for consistently describing ground and excited states on the same quantum mechanical level. Based on our implementation in the all-electron localized basis code FHI-aims [1], we show that for finite systems self-consistent GW reaches the same final Green function regardless of the starting point. The results show that self-consistency systematically improves ionization energies and total energies of closed shell systems compared to perturbative GW calculations (G_0W_0) based on Hartree-Fock or (semi)local density-functional theory. These improvements also translate to the electron density as demonstrated by a better description of the dipole moments of hetero-atomic dimers and the similarity with the coupled cluster singles doubles (CCSD) density. The starting-point independence of the self-consistent Green function facilitates a systematic and unbiased assessment of the performance of the GW

approximation for finite systems. It therefore constitutes an unambiguous reference for the future development of vertex corrections and beyond GW schemes.

[1] V. Blum *et al.*, *Comp. Phys. Comm.* **180**, 2175 (2009).

Topical Talk

O 84.8 Fri 12:30 HE 101

Density-functional theory - time to move on? — ●NICOLA MARZARI — Theory and Simulations of Materials, École Polytechnique Fédérale de Lausanne

Density-functional theory can be a very powerful tool for scientific discovery and technological advancement. Still, it remains an imperfect tool, with open and urgent challenges in our quest towards qualitative and quantitative accuracy, and in our ability to perform quantum simulations under realistic conditions.

Several of these challenges stem from the remnants of self-interaction in our electronic-structure framework, leading to qualitative failures in describing some of the fundamental processes involved in energy applications - from charge-transfer excitations to photoemission spectra, to the structure and reactivity of transition-metal complexes.

I'll discuss these challenges in realistic case studies, and our suggestions for possible solutions - including constrained DFT, DFT + onsite and intersite Hubbard terms, and Koopmans' compliant energy functionals. In particular, I'll discuss how self-interaction corrected functionals lead naturally to a beyond-DFT formulation where both total energies and spectroscopic properties can be accounted for.