

TT 22: Focused Session: Frontiers of Electronic Structure Theory 2 (jointly with HL and O)

Time: Monday 16:00–19:15

Location: H36

TT 22.1 Mon 16:00 H36

Excited States of the divacancy in SiC — ●MICHEL BOCKSTEDTE¹, THOMAS GARRATT¹, and ADAM GALI² — ¹Theoretische Festkörperphysik, FAU Erlangen-Nürnberg, Staudstr. 7B2, D-91058 Erlangen — ²Wigner Research Centre for Physics, Hungarian Academy of Sciences, PO Box 49, Budapest 1525, Hungary

The negatively charged nitrogen-vacancy center in diamond has emerged as a candidate for the implementation of a qubit in quantum computing. Silicon Carbide also fulfills necessary conditions¹ which makes it a suitable material for this purpose. With the neutral divacancy it possess a defect center with a high spin ground state, which can be manipulated by spin-resonance techniques.² Optical excitation of the triplet ground state and subsequent spin-selective recombination via yet unknown intermediate spin-singlet states enables spin-initialization with $M_z=0$, which is requisit for a qubit. Here we investigate the excitation spectrum of the divacancy based *ab initio* methods. DFT and TD-DFT calculations³ reveal a Jahn-Teller effect for the first excited triplet state that is absent for the NV-complex. TD-DFT and an *ab initio* many body hamiltonian nicely reproduce the prominent photoluminescence transitions. The latter method also describes the spin-singlet states. We discuss the defect excitation spectrum in the light of the Jahn-Teller distortion.

[1] J. R. Weber *et al.*, PNAS **107**, 8513 (2010).

[2] F. Koehl *et al.*, Nature **479**, 84 (2011).

[3] A. Gali, phys. status solidi (b) **248**, 1337 (2011).

TT 22.2 Mon 16:15 H36

Extending the random phase approximation for electronic correlation energies: The renormalized adiabatic local density approximation — ●THOMAS OLSEN — Technical University of Denmark

The adiabatic connection fluctuation-dissipation theorem with the random phase approximation (RPA) has recently been applied with success to obtain correlation energies of a variety of chemical and solid state systems. The main merit of this approach is the improved description of dispersive forces while chemical bond strengths and absolute correlation energies are systematically underestimated. In this work we extend the RPA by including a parameter-free renormalized version of the adiabatic local density (ALDA) exchange-correlation kernel. The renormalization consists of a (local) truncation of the ALDA kernel for wave vectors $q > 2k_F$, which is found to yield excellent results for the homogeneous electron gas. In addition, the kernel significantly improves both the absolute correlation energies and atomization energies of small molecules over RPA and ALDA. The renormalization can be straightforwardly applied to other adiabatic local kernels.

TT 22.3 Mon 16:30 H36

First-principles IXS spectra for TiO₂ and HfO₂ — ●LINDA HUNG and FRANCESCO SOTTILE — Ecole Polytechnique, Palaiseau, France

Using time-dependent DFT and many-body perturbation theory, we determine the inelastic x-ray scattering (IXS) spectra for bulk TiO₂ and HfO₂. Excitations from valence and semi-core states are modeled, corresponding to transition energies up to 60 eV. By varying momentum transfer, plasmon dispersion can be observed. We characterize differences in the spectra for the rutile, anatase, and brookite polymorphs of TiO₂, as well as the cubic, tetragonal, and orthogonal polymorphs of HfO₂. These spectra are also Fourier transformed, allowing us to image the real-time and real-space electron density response to external perturbations.

TT 22.4 Mon 16:45 H36

Linear-scaling time dependent density-functional theory in the linear response formalism — ●TIM J. ZUEHLSDORFF, NICHOLAS D. M. HINE, JAMES S. SPENCER, NICHOLAS M. HARRISON, and PETER D. HAYNES — Imperial College London, UK

In recent years, linear-scaling approaches to density-functional theory have enabled the computation of ground-state properties of large nanostructures and biomolecules. While these methods are now well established, the linear-scaling computation of excited state properties via time-dependent density-functional theory (TDDFT) in the linear response regime is less developed.

In this talk we will present an implementation of TDDFT in the linear response formalism, enabling the computation of low-energy optical absorption spectra for large molecules and nanostructures. The method avoids any explicit reference to canonical representations of either occupied and unoccupied Kohn-Sham states and thus achieves linear-scaling computational effort with system size. In contrast to conventional localised orbital formulations where a single basis set is used to represent the occupied and unoccupied Kohn-Sham states, we make use of two sets of in-situ optimised localised orbitals, one for the occupied and one for the unoccupied Kohn-Sham space. The double basis set approach avoids known problems of representing the unoccupied space with localised orbitals optimised for the occupied space, while the in-situ optimisation procedure allows for efficient calculations with a minimal set of basis functions. The method is applied to a number of large-scale test systems in order to demonstrate its validity.

TT 22.5 Mon 17:00 H36

Dynamical spin and charge excitations with spin-orbit coupling in 3d adatoms on Cu(111) and Pt(111) — ●MANUEL DOS SANTOS DIAS, BENEDIKT SCHWEFLINGHAUS, and SAMIR LOUNIS — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany

The presence of spin-orbit coupling has a fundamental impact on the magnetic excitation spectrum: there is a finite gap at zero frequency and spin and charge excitations become coupled. The excitation spectrum is derived from the dynamical magnetic susceptibility of the electronic system, for which we developed a formalism based on Time-Dependent Density Functional Theory, as implemented in the Korringa-Kohn-Rostoker Green function method [1,2]. As an application, we present first-principles calculations of the charge, longitudinal and transverse magnetic excitations of 3d adatoms deposited on the Cu(111) and Pt(111) surfaces. Focus is on the expected spin-charge coupling induced by the spin-orbit interaction, and on the dynamical anisotropic effects that generalize the familiar magnetic anisotropy.

Work supported by the HGF-YIG Programme FunSiLab – Functional Nanoscale Structure Probe and Simulation Laboratory (VH-NG-717).

[1] S. Lounis, A. T. Costa, R. B. Muniz and D. L. Mills, Phys. Rev. Lett. **105**, 187205 (2010)

[2] S. Lounis, A. T. Costa, R. B. Muniz and D. L. Mills, Phys. Rev. B **83**, 035109 (2011)

TT 22.6 Mon 17:15 H36

Beyond the GW approximation: a second-order screened exchange correction — ●PATRICK RINKE¹, XINGUO REN¹, NOA MAROM², FABIO CARUSO¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz Haber Institute, Berlin, Germany — ²University of Texas, Austin, USA

Despite the success of the GW method in describing the photoemission spectra of solids, molecules and clusters, challenges remain. For aromatic molecules for example absolute as well as relative positions of ionisation energies and affinities are not well reproduced in perturbative G_0W_0 schemes with different starting points as well as in self-consistent GW [1], sometimes even giving the wrong orbital order. Motivated by renormalized second-order perturbation theory [2] for the ground-state energy, we propose a second-order screened exchange correction (SOSEX) to the GW self-energy. This correction follows the spirit of the SOSEX correction to the random-phase approximation for the electron correlation energy and reduces the self-correlation error. The performance of the GW+SOSEX scheme has been benchmarked for a set of molecular systems, including the G2 set, commonly used acceptor molecules, benzene and the azabenzene molecules. We find that the SOSEX correction improves the description of the spectral properties including the orbital order with respect to the different GW schemes, highlighting the importance of reducing the self-correlation error. [1] N. Marom *et al.*, arXiv:1211.0416 [2] X. Ren *et al.*, J. Mater. Sci. **47**, 7447 (2012)

TT 22.7 Mon 17:30 H36

A strategy for finding a reliable starting point for G_0W_0 demonstrated for molecules — ●THOMAS KÖRZDÖRFER¹ and NOA

MAROM² — ¹Institut für Chemie, Universität Potsdam, D-14476 Potsdam — ²Center for Computational Materials, Institute of Computational Engineering and Sciences, The University of Texas at Austin, Austin, TX 78712, USA

Many-body perturbation theory in the G_0W_0 approximation is an increasingly popular tool for calculating electron removal energies and fundamental gaps for molecules and solids. However, the predictive power of G_0W_0 for molecules is limited by its sensitivity to the density functional theory (DFT) starting point. In this contribution, the starting point dependence of G_0W_0 is demonstrated for several organic molecules. Analysis of the starting point dependence leads to the development of a non-empirical scheme that allows to find a consistent and reliable DFT starting point for G_0W_0 calculations by adapting the amount of Hartree-Fock-exchange in a hybrid DFT functional. The G_0W_0 spectra resulting from this *consistent starting point (CSP) scheme* [1] reliably predict experimental photoelectron spectra over the full energy range. This is demonstrated for a test set of various typical organic semiconductor molecules.

[1] T. Körzdörfer and Noa Marom, Phys. Rev. B Rapid Communications **86**, 041110 (2012).

TT 22.8 Mon 17:45 H36

Electronic properties of isolated and supported organic dyes modeled through the GW method — ●PAOLO UMARI¹, FILIPPO DE ANGELIS², LUIGI GIACOMAZZI³, MARIACHIARA PASTORE², and STEFANO BARONI³ — ¹Dipartimento di Fisica e Astronomia, Università di Padova, Italy — ²Istituto CNR di Scienze e Tecnologie Molecolari, Perugia, Italy — ³Scuola Internazionale Superiore di Studi Avanzati (SISSA), Trieste, Italy

The first-principles GW method is used for investigating the electronic levels of isolated and supported dyes for electrochemical solar cells. We consider a set of all-organic dyes, (L0,L2,L3,L4) exhibiting the same donor and anchor groups. First, we calculate the energy levels in the limit of isolated molecules obtaining nice agreement with available experimental photoelectron spectra. Then, we consider the L0 and the L2 dyes while adsorbed on the anatase TiO₂ (101) surface. Also in this case we find good agreement when comparing with available experimental photoelectron spectra. We find that the HOMO -LUMO gap of the dye is reduced with respect to the isolated molecule and that the HOMO level is slightly shifted towards higher energies due to image charge effects. This permits us to derive a simple model for obtaining approximate GW energy levels for the HOMO and the LUMO of the adsorbed molecule and for the valence band maximum and the conduction band minimum of the substrate performing just one complete GW calculation of the isolated molecule and one of the bulk TiO₂ combined with a calculation at the DFT level of the adsorbed molecule complex. In this way, we can investigate larger, more realistic, model structures.

TT 22.9 Mon 18:00 H36

Ab-initio description of satellites in semiconductors — ●MATTEO GUZZO^{1,2}, JOSH J. KAS³, LORENZO SPONZA^{1,2}, CHRISTINE GIORGETTI^{1,2}, FRANCESCO SOTTILE^{1,2}, DEBORA PIERUCCI⁴, MATHIEU G. SILLY⁴, FAUSTO SIROTTI⁴, JOHN J. REHR³, and LUCIA REINING^{1,2} — ¹LSI, Ecole Polytechnique, Palaiseau, France — ²European Theoretical Spectroscopy Facility (ETSF) — ³UW, Seattle, USA — ⁴Synchrotron Soleil, Gif-sur-Yvette, France

The GW method from Many-Body Perturbation Theory 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. Including additional diagrams in the Green's function we obtain an excellent description of satellites series in the test case of bulk silicon, where GW is unable to cope [1]. This approach can be extended to more complex system, i.e. graphite. 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 true freestanding graphene. [1] M. Guzzo et al., Phys. Rev. Lett. **107**, 166401 (2011)

TT 22.10 Mon 18:15 H36

Optical spectra of alkali-metal fluorides — ●CHRISTOPH SOMMER, PETER KRÜGER, and JOHANNES POLLMANN — Institut für Festkörpertheorie, Universität Münster, D-48149 Münster, Germany

We have studied the virtue of different approximations for quasiparticle energies in the calculation of optical spectra including excitonic effects by solving the Bethe-Salpeter equation (BSE). To this end, we have computed exemplarily optical spectra of the three alkali-metal fluorides LiF, NaF, and KF using quasiparticle energies resulting from two different approximations of the self-energy operator in Hedin's GW approach as well as electronic energies and wave functions obtained by employing self-interaction corrected pseudopotentials. The energetic positions of characteristic peaks in the calculated and measured spectra are in very good agreement when quasiparticle energies are used that result after an update of the screened interaction W on the basis of a preceding G_0W_0 calculation. Additionally, two simple further approximations for one-particle energies that use input either from experiment or from quasiparticle calculations for a small set of wave vectors are included into this investigation.

TT 22.11 Mon 18:30 H36

Bethe-Salpeter Equation from many-body perturbation theory — ●TOBIAS SANDER, RONALD STARKE, and GEORG KRESSE — Computational Materials Physics, University of Vienna, Sensengasse 8/12, 1090 Vienna, Austria

The Green function formalism is a powerful tool to calculate not only electronic structure within the quasi-particle (QP) picture, but it also gives access to optical absorption spectra. Starting from QP energies within the GW method, the polarizability, as central quantity, is calculated from the solution of a Bethe-Salpeter-like equation (BSE). It is usually solved within the Tamm-Dancoff Approximation (TDA) which neglects the coupling of resonant (positive frequency branch) and anti-resonant (negative frequency branch) excitations. In this work we solve the full BSE [1] (beyond TDA) based on self-consistently calculated QP orbitals and energies [2] for typical systems. The dielectric function is averaged over many low dimensional shifted \mathbf{k} -meshes to obtain \mathbf{k} -point converged results. We compare the results to recently introduced approximation to the BSE kernel [3]. Additionally, the time-evolution ansatz [4] is employed to calculate the polarizability, which avoids the direct solution of the BSE.

[1] S. Albrecht, L. Reining, R. Del Sole, G. Onida, PRL **80**, 4510 (1998)

[2] M. Shishkin, M. Marsman, G. Kresse, PRL **99**, 246403 (2007)

[3] L. Reining, PRL **88**, 66404 (2002)

[4] W. G. Schmidt, S. Glutsch, P. H. Hahn, F. Bechstedt, PRB **67**, 085307 (2003)

TT 22.12 Mon 18:45 H36

Acceleration of the response function convergence using the effective energy techniques within the ultrasoft pseudopotential and PAW methods — ●JIRÍ KLIMEŠ and GEORG KRESSE — Faculty of Physics, University of Vienna, A-1090 Vienna, Austria

Calculations of quasiparticle spectra based on the GW approximation or evaluation of total energies using the RPA method are of a wide interest in the computational materials community. However, their applicability is to a large extent limited by the cost of evaluating the response function or the selfenergy where a large number of unoccupied bands needs to be included. A promising way to speed-up the convergence is to use the resolution of identity and replace the sum over an infinite number of unoccupied states by an effective correction [1,2]. However, the available schemes have been only formulated for norm-conserving pseudopotentials and when applied directly within the ultrasoft pseudopotentials (USPPs) or the PAW method they introduce an error since the correction term doesn't vanish when the number of included bands is increased. Here we present an implementation of the schemes within the formalism of USPPs or the PAW method which gives the proper behaviour of the correction term. We also show how the convergence of the scheme given in [2] can be further improved and discuss the efficiency of the methods for RPA total energy calculations.

[1] F. Bruneval and X. Gonze, PRB **78**, 085125 (2008)

[2] J. A. Berger, L. Reining, and F. Sottile, PRB **82**, 041103(R) (2010); PRB **85**, 085126 (2012)

TT 22.13 Mon 19:00 H36

SnO: GW band gap of a van der Waals bonded system — ●KIRSTEN GOVAERTS¹, ROLANDO SANIZ², BART PARTOENS², and

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In this work we have investigated the structural and electronic properties of SnO, which is built up by layers kept together by van der Waals

(vdW) forces. The combination of a vdW functional (within DFT) and GW calculations leads to accurate values for the c/a ratio and the fundamental band gap. A comparison is made between three starting points for the GW calculation: a regular PBE calculation, one with the vdW effect included, and a hybrid functional calculation. The difference between different levels of self-consistency is also investigated.