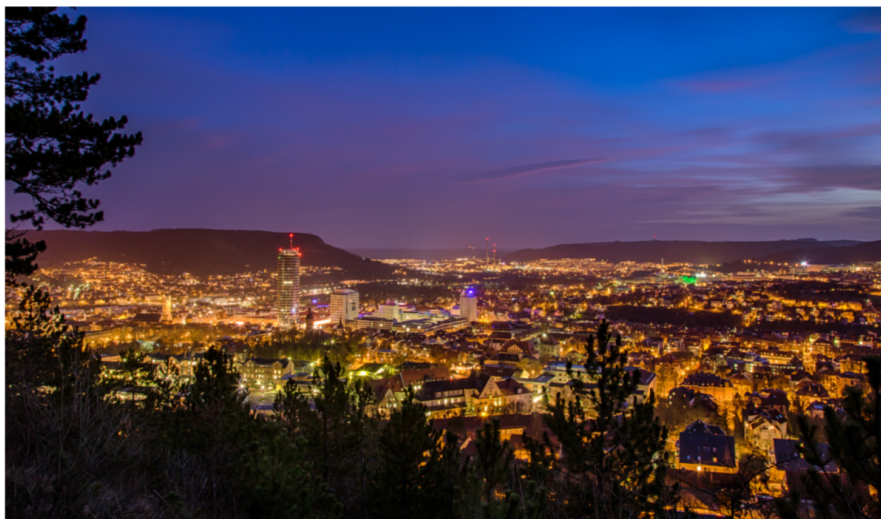




24th ETSF Workshop on Electronic Excitations

**Light-Matter Interaction and Optical Spectroscopy
from Infrared to X-Rays**



Jena, Germany

16 – 20 September 2019

Welcome

The workshop series of the European Theoretical Spectroscopy Facility (ETSF) provides a forum for excited states and spectroscopy in condensed-matter physics, chemistry, nanoscience, materials science, and molecular physics attracting theoreticians, code developers, and experimentalists alike.

Light-matter interaction will be at core of the 2019 edition of the ETSF workshop. Cutting-edge spectroscopy experiments allow to probe electrons, plasmons, excitons, and phonons across different energy and time scales with unprecedented accuracy. A deep physical understanding of the underlying quantum many-body effects is of paramount importance to analyze experimental observations and render theoretical simulations predictive. The workshop aims at discussing the most recent advances in the theoretical description of the interaction between light and matter focusing on first-principles methods. This broad subject will be covered in its diverse declinations, from core-level spectroscopy to collective low-energy excitations, discussing also matter under extreme conditions, and systems driven out of equilibrium by strong laser pulses.

Exchange between theorists and experimentalists is fostered to open new horizons towards the next generation of novel spectroscopy techniques. The workshop will also face the challenges posed by the formidable complexity of heterogeneous and nanostructured systems such as those of interest for light harvesting and energy generation, prompting to bridge the gap between experimental and *in silico* spectroscopy.

Workshop topics include:

- Linear and nonlinear optical spectroscopy
- Core-level spectroscopies
- Ultrafast excitation dynamics
- Electron-phonon coupling
- Light harvesting in natural and synthetic systems

We are glad to welcome you in Jena, the city of light, and wish you an inspiring workshop with lots of interesting science and fruitful discussions.

The organizers

General information

ETSF workshop team (Organizing and program committee)

- Claudia Rödl (Friedrich-Schiller-Universität Jena, Jena, Germany)
- Gabriele D'Avino (Institut Néel, CNRS, Grenoble, France)
- Michiel van Setten (IMEC, Leuven, Belgium)
- Guido Fratesi (Università degli Studi di Milano, Milan, Italy)
- Elena Cannuccia (Università degli Studi di Roma "Tor Vergata", Rome, Italy)
- Carina Faber (UCLouvain, Louvain-la-Neuve, Belgium)

Local committee

- Claudia Rödl (Friedrich-Schiller-Universität Jena, Germany)

ETSF steering committee

The ETSF steering committee (SC) consists of nine elected research team leaders (RTLs). The current SC members are:

- Matthieu Verstraete (Université de Liège, Liège, Belgium), Chair
- Claudio Attaccalite (Aix-Marseille Université, Marseille, France)
- Arjan Berger (Université Paul Sabatier, Toulouse, France)
- Letizia Chiodo (Università Campus Bio-Medico di Roma, Rome, Italy)
- Rex Godby (University of York, York, UK)
- Myrta Grüning (Queen's University Belfast, Belfast, UK)
- Gian-Marco Rignanese (UCLouvain, Louvain-la-Neuve, Belgium)
- Francesco Sottile (École polytechnique, Palaiseau, France)
- Zeila Zanolli (ICN2, Barcelona, Spain)

Support

The organizers acknowledge financial support from the Friedrich-Schiller-Universität Jena, the Ψ_k Network, the Michael Stifel Center Jena, the Abbe Center of Photonics, the SFB "NOA - Non-linear Optics Down to Atomic Scales", and jenaparadies.

Workshop venue

The workshop is hosted by the **Friedrich-Schiller-Universität Jena** in the historical **Rosensäle** conference building in the very center of Jena (Fürstengraben 27, first floor).

The **lecture room** (“Großer Sitzungssaal”, room no. 102) is located on the first floor. Another directly adjacent room (“Seminarraum”, room no. 103) is available as workspace for the participants. The poster session and the coffee breaks are held in the “Kleiner Sitzungssaal” (room no. 101).

Conference desk

The conference desk is located in the entrance hall in front of the “Großer Sitzungssaal” (room no. 102) on the first floor.

Internet access

Wi-fi is available in all university buildings via “eduroam”. Credentials are provided at the registration desk.

Poster session with barbecue

The poster boards are situated in the “Kleiner Sitzungssaal” (room no. 101). Posters can already be put up on Monday. Posters must be taken down by the coffee break on Friday morning. During the poster session, a Thuringian barbecue will be organized in the backyard of the conference building. To reach the backyard, please follow the signs.

Coffee breaks and lunches

Coffee, tea, drinks, and snacks will be available in the “Kleiner Sitzungssaal” (room no. 101) during the morning (at 10:20) and afternoon (at 15:30) **coffee breaks**.

Lunch will be served at 12:30 in different restaurants within the city center (upon presentation of the conference badge):

- Tuesday: Gaststätte “Zur Noll”, Oberlauengasse 19
- Wednesday: Wirtshaus Ratszeise, Markt 1
- Thursday: L'Osteria Jena, Leutragraben 1

Social program

On Monday, a **welcome evening** with drinks and finger food is organized at the **Theatercafé** (Schillergässchen 1) giving the participants the opportunity to meet in a casual atmosphere. The welcome reception starts at 19:00.

The workshop participants may join a **guided tour of the city center of Jena** after the scientific

program on Thursday. The meeting point is the tourist information at the market (Jena Tourist-Information, Markt 16). The guided tour will end in front of the restaurant where the social dinner takes place. We have booked two English-speaking and one German-speaking guide and ask German speakers to preferentially join the German-speaking tour.

The **social dinner** on Thursday will take place at the **restaurant “Zur Noll”** (Oberlauengasse 19) in the city center. The dinner starts at 19:00.

Participants interested in these events will be asked to confirm their participation during the meeting.

Transportation

The workshop venue, lunch restaurants, train stations, suggested hotels, and some suggested restaurants (not endorsed by the organization) are within walking distance in the historical city center. In principle, public transport is not needed to get around during the workshop.

If, however, you want to visit the outskirts, information on trams and buses (that run all night, although with reduced frequency) is available on the website of the **public transport company JeNah** (<https://www.nahverkehr-jena.de/>). Tickets can be bought at the ticket machines at (some) stops, in the service center (Holzmarkt-Passage, Holzmarkt 1), or with a dedicated mobile app. Single-ride tickets cost 2.10 €, four-ride tickets 7.60 €.

Program

	Monday, 16 September
13:30	ETSF steering committee meeting
15:30	<i>Registration & coffee</i>
16:00	Opening
	Introductory lectures
16:10	Lucia Reining – Fingerprints of correlation in electronic spectra of materials: How can calculations help to understand and make predictions?
16:55	Matthias Scheffler – Thermal and electrical conductivity to all orders in electron-phonon and phonon-phonon coupling
19:00	Welcome evening with drinks and finger food

	Tuesday, 17 September
	Light-matter interaction and electron-phonon coupling
09:00	Emmanouil Kioupakis – Phonon-mediated quantum processes in materials
09:40	Lorenzo Sponza – <i>Ab-initio</i> simulations, semi-empirical methods and experiments unveiling the optical properties of boron nitride
10:00	Friedhelm Bechstedt – Out-of-plane excitons in 2D crystals
10:20	<i>Coffee break</i>
10:50	Bernhard Urbaszek – Excitonic properties and spin-valley dynamics of 2D materials
11:30	Pedro Melo – Optical absorption of defected WS ₂ monolayers
11:50	Philipp Marauhn – Effect of layer thickness on electronic excitations in TMDCs
12:10	<i>Lunch</i>
	Electronic-structure methods I: Correlation
14:10	Pina Romaniello – Photoemission Spectra beyond GW: The Band Gap in Strongly Correlated Systems
14:50	Savio Laricchia – Electron-phonon coupling within quasiparticle self-consistent GW
15:10	Martin Panholzer – Beyond Kohn-Sham DFT: Explicitly correlated wave functions
15:30	<i>Coffee break</i>
16:00	Charles H. Patterson – Density fitting approach to many-body calculations in molecules and solids
16:20	Nicole Helbig – Correlation and localization in reduced density-matrix functional theory
16:40	Poster session with Thuringian barbecue

	Wednesday, 18 September
	Linear and nonlinear optics
09:00	Myrta Grüning – Nonlinear optics from first-principles real-time approaches
09:40	Valérie Vénard – Optical nonlinear processes in semiconductors in the presence of a DC field: An <i>ab-initio</i> description
10:00	Thorsten Deilmann – Properties of electron-hole excitations: Screened exchange interaction and <i>Q</i> -resolved exciton band structure
10:20	<i>Coffee break</i>
	The XC potential revisited
10:50	Ayoub Aouina – The connector theory: New approximations for the exchange-correlation potential
11:10	Rex Godby – New approaches to TDDFT exchange-correlation kernels for theoretical spectroscopy
11:30	ETSF General Meeting
12:10	<i>Lunch</i>
	Light harvesting and optoelectronic applications
14:10	Koen Vandewal – Inter-molecular charge-transfer states for organic optoelectronics
14:50	Frank Ortmann – Vibrations and their Impact on Absorption Spectra: Shaping Excitons in Organic Materials
15:10	Claudio Quarti – Optical response of layered hybrid lead halide perovskites: A complex interplay of dielectric confinement, electron-phonon coupling and point defects
15:30	<i>Coffee break</i>
16:00	Roberta Poloni – Photoactive metal-organic frameworks for efficient gas separation
16:20	Marco Gruenewald – Optical <i>in situ</i> spectroscopy of ultrathin organic films
16:40	Jens Renè Suckert – A SiGe nanolaser, is it possible?
17:00	<i>Break</i>
	Evening talks
17:15	Gerhard G. Paulus – Non-invasive cross-sectional imaging of semiconductors with nanoscale resolution
17:45	Christian Eggeling – Challenges and potentials: Experiences from super-resolution microscopy in biomedical research

	Thursday, 19 September
	Ultrafast phenomena I: Photoemission
09:00	Luca Perfetti – Time resolved electrons dynamics in layered semiconductors
09:40	Eugene E. Krasovskii – Attosecond spectroscopy of crystals: Wigner delay, Hartman effect, and external fields
10:00	Felix Otto – Photoelectron momentum maps (PMMs): A tool to investigate molecular properties
10:20	<i>Coffee break</i>
	Ultrafast phenomena II: Excitons
10:50	Davide Sangalli – <i>Ab initio</i> description of pump and probe experiments: From carriers to exciton dynamics
11:30	Antonios M. Alvertis – Exciton temperature dependence dictated by localisation in organic semiconductors
11:50	Hsiao-Yi Chen – <i>Ab Initio</i> Exciton Dynamics and Radiative Recombination
12:10	<i>Lunch</i>
	Electronic-structure methods II: Optics
14:10	Stefanie Gräfe – Interaction of intense laser fields with matter
14:50	Jaakko Koskelo – Dielectric function of homogeneous electron gas from Bethe-Salpeter equation
15:10	Christine Giorgetti – Optical properties in thin layer materials
15:30	<i>Coffee break</i>
	Magnetism
16:00	Christoph Friedrich – Electron-Magnon Scattering from First Principles within the <i>GT</i> and <i>GWT</i> Self-Energies
16:20	Beata Taudul – XAS as a powerful tool for rationalizing electrochemical processes in Li/Na-ion batteries
17:30	Guided tour
19:00	Workshop dinner

	Friday, 20 September
	Core-level and x-ray spectroscopy
09:00	Claudia S. Schnohr – X-ray absorption spectroscopy of semiconductors alloys
09:40	Hazem Aldahhak – Unraveling the oxidation state of manganese corrols on Ag(111)
10:00	Vasil Rokaj – QED-Bloch Theory with Homogeneous Magnetic Fields: Modifications of the Landau Levels and the Hofstadter Butterfly
10:20	<i>Coffee break</i>
10:50	Caterina Cocchi – All-electron many-body perturbation theory for core spectroscopy in organic, inorganic, and hybrid materials
11:30	Igor Reshetnyak – <i>Ab initio</i> calculation of the band-gap of liquid water: Insight from spectroscopy
11:50	Christian Vorwerk – Electron-Hole Correlation in Resonant Inelastic X-ray Scattering of Solids
12:10	Closing remarks

Oral contributions

Fingerprints of correlation in electronic spectra of materials: How can calculations help to understand and make predictions?

Lucia Reining^{1,2}

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²*European Theoretical Spectroscopy Facility (ETSF)*

Many properties of materials are determined by electronic excitations. However, in a piece of matter an electron is never excited alone, since electrons cannot be distinguished and since the Coulomb interaction is strong and long-ranged. In general an excitation involves the entire system, including classical electrostatic and purely quantum mechanical contributions. How can theory understand, and how can calculations predict, the wealth of unexpected phenomena that may take place?

In this talk we will see how first principles calculations contribute to our understanding, focusing on the main theoretical concepts, recent progress, and comparison with experiment.

We will conclude with some open questions and challenges.

Thermal and electrical conductivity to all orders in electron-phonon and phonon-phonon coupling

Matthias Scheffler¹

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Thermal conductivity (TC) is a key characteristic of many materials, e.g. thermo-electrics, thermal-barrier coatings, catalysts. However, TC is largely unknown – of the 225,000 identified inorganic semiconductor and insulator crystals, only 100 have any TC data available. We developed and coded a full *ab initio* molecular dynamics description of TC with a numerically efficient algorithm that enables convergence of the statistical mechanics in system size and time. Together with a “rapid decision algorithm” on what materials actually exhibit strong anharmonic effects and thus low TCs, we find that in many of the technologically interesting materials anharmonic effects are large, so that the standard description in terms of perturbation theory and Boltzmann equation does not provide a reliable description. Somewhat analogously, we developed an *ab initio* theory of electrical transport that does not involve perturbation theory and/or the quasi-harmonic approximation but treats the electron-phonon coupling and anharmonic effects to all orders.

Phonon-mediated quantum processes in materials

Emmanouil Kioupakis¹

¹ *University of Michigan, USA*

Lattice vibrations play an important role in mediating quantum processes in materials that control the operation of electronic and optoelectronic devices. In this talk I will discuss the methodology and results of predictive atomistic calculations of phonon-mediated quantum processes in materials based on density functional and many-body perturbation theory. I will discuss phonon-assisted optical absorption in metals and in indirect-gap semiconductors such as silicon (Si), boron arsenide (BAs), and boron nitride (BN). I will also discuss Auger recombination in wide-band-gap semiconductors, an important nonradiative mechanism that dominates carrier recombination at high free-carrier concentrations. The results shed light into the interaction of light with materials and the efficiency of light-emitting devices.

This work was performed in collaboration with Kyle Bushick, Kelsey Mengle, Chris Van de Walle, and Andrew McAllister. It was supported by NSF awards 1254314 (DMR/CMMT CAREER program) and 1534221 (DMREF program). Computational resources were provided by the DOE NERSC facility.

***Ab-initio* simulations, semi-empirical methods and experiments unveiling the optical properties of boron nitride**

L. Sponza,¹ L. Schué,^{1,2} F. Fossard,¹ H. Amara,¹ S. Latil,³ C. Attacalite,⁴ F. Ducastelle,¹
A. Loiseau,¹ and J. Barjon²

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Hexagonal boron nitride (hBN) is a semiconductor with a wide indirect gap. It displays peculiar optical properties, including a phonon-assisted emission with an unexpectedly intense luminescence, and a puzzling asymmetry between emission and absorption spectra.

In this presentation, I will report on some recent investigations on this subject [1,2,3] combining experimental and theoretical investigations. I will report on the excitonic dispersion in monolayer and bulk hBN, computed by solving the finite-q Bethe-Salpeter equation both from first principles and with a purposely derived tight-binding model [2]. The comparison against an independent-particle model will allow me to highlight a strong q-dependency of the exciton binding energy which provides a key element to unveil the origin of the asymmetry between absorption and emission spectra [3].

[1] L. Sponza, H. Amara, F. Ducastelle, A. Loiseau, and C. Attacalite, Phys. Rev. B **97**, 075121 (2018)

[2] L. Sponza, H. Amara, C. Attacalite, S. Latil, T. Galvani, F. Paleari, L. Wirtz, and F. Ducastelle, Phys. Rev. B **98**, 125206 (2018)

[3] L. Schué, L. Sponza, A. Plaud, H. Bensalah, K. Watanabe, T. Taniguchi, F. Ducastelle, A. Loiseau, and J. Barjon, Phys. Rev. Lett **122**, 067401 (2019)

Out-of-plane excitons in 2D crystals

I. Guillhon,¹ M. Marques,¹ L. K. Teles,¹ M. Palummo,² O. Pulci,² Silvana Botti,³ and F. Bechstedt³

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Two-dimensional (2D) materials are ideal platforms to explore new physical phenomena and reveal unique optical properties. The reduced screening strongly enhances the excitonic and quasiparticle effects. The response to a perturbing electromagnetic field is dominated by in-plane light polarization. However, out-of-plane pair excitations are still allowed despite of the quantum confinement of the atomic sheets in normal direction. The optical properties on the considered directions are also ruled by selection rules and local-field effects [1]. We use the state-of-art GW approximation and the Bethe-Salpeter equation to investigate optical transitions for light polarization both parallel and normal to the atomic planes. Graphene (Gr), graphene oxide (GO), boron nitride (BN), and molybdenum disulfide (MoS₂) are investigated as prototypical systems with honeycomb structure, ranging from semimetals to large-gap insulators. The two components of the optical conductivity are computed and the observed anisotropy is discussed in terms of fundamental gap size and effective sheet thickness. The two peaks of the real part of the in-plane 2D optical conductivity at 5.8 eV and 6.6 eV are the signature of the first and second bound exciton of BN [2], while the first allowed excitons for out-of-plane light polarization appear at 9.35 eV. The very large blueshift of optical absorbance edge is also observed for Gr, the other one-atom thick considered 2D crystal. For few-atomic thick materials, GO and MoS₂, the blueshift is less intense. The intensity of the out-of-plane optical conductivity is reduced by orders of magnitude, in agreement with recent measurements [3].

[1] A. Marinopoulos, L. Wirtz, A. Marini, V. Olevano, A. Rubio, and L. Reining, *Applied Physics A* **78**, 1157 (2004).

[2] L. Wirtz, A. Marini, and A. Rubio, *Phys. Rev. Lett.* **96**, 126104 (2006).

[3] J. P. Echeverry, B. Urbaszek, T. Amand, X. Marie, and I. C. Gerber, *Phys. Rev. B* **93**, 121107 (2016).

Excitonic properties and spin-valley dynamics of 2D materials

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The optical properties of transition metal dichalcogenide (TMD) monolayers (MLs) such as MoS₂ and WSe₂ are dominated by excitons, electron and hole pairs bound by Coulomb attraction [1]. In this talk we report recent results on linear and non-linear optical spectroscopy of these atomically thin semiconductors for applications in optoelectronics and spintronics. We discuss fundamental parameters such as the optical bandgap and the photoluminescence emission time and yield that can be tuned by changing the dielectric environment of the monolayers and using different substrate materials and heterostructure fabrication techniques. We discuss the polarization dynamics of excitons and resident carriers in different TMD materials giving access to spin and valley physics.

[1] G.Wang, A. Chernikov, M.M. Glazov, T. Heinz, X. Marie, T. Amand and B. Urbaszek, *Rev. Mod. Phys.* **90**, 021001 (2018).

Optical absorption of defected WS₂ monolayers from first principles

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Transition metal dichalcogenides (TMDs) have shown to be strong contenders as components in optical devices. Mostly this derives from the fact that spin and valley degrees of freedom are coupled together. This allows us to use circularly polarised electric fields to select the region in the Brillouin zone where optical transitions take place. However, synthesis of large pristine samples is still out of reach and are usually produced with atomic vacancies or substitutions.

These defects will inevitably alter the optical properties of the sample by changing its bandstructure (e.g. rising of mid gap states) or the spin-texture of the bands. Here we present our first principle calculations of absorption spectra of defected WS₂ monolayers, obtained by combining both GW and BSE methods. By introducing vacancies and atomic replacements in large supercells, we are able to study how ground state and optical phenomena are changed.

We can then link the new spectral features to the changes introduced by the defects.

Effect of layer thickness on electronic excitations in TMDCs

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Transition metal dichalcogenides (TMDCs) attract a lot of attention due to their unique optoelectronic properties. Here, we discuss effects on the excited states that arise when stacking atomically thin monolayers into multilayer or bulk systems. We investigate the spectral properties of TMDCs by employing many-body perturbation theory. For this, we solve the Bethe-Salpeter equation on top of a preceding LDA+ GdW calculation. Our results show spectral shifts with increasing number of layers. These shifts can largely be attributed to the change in screening. Stacking layers on top of each other results in an enhanced screening environment shifting the excitons towards lower energy. This redshift is also observed in experiment [1]. Another significant effect of stacking is that new types of excitons occur. In a monolayer, electron and hole can only form intralayer excitons. In multilayer or bulk systems, on the other hand, the electron and the hole can also form interlayer excitons, in which the two particles reside on different layers.

[1] Y. Niu et al., *Nanomaterials*, **8**, 725 (2018)

Photoemission Spectra beyond GW: The Band Gap in Strongly Correlated Systems

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²*European Theoretical Spectroscopy Facility*

Photoemission is a powerful tool to obtain insight into the electronic structure and excitations in materials. From the theoretical point of view Many-Body Perturbation Theory, within the so called GW approximation to electron correlation, is the method of choice for calculations of photoemission spectra of many materials. However GW suffers from some fundamental shortcomings, and, in particular, it does not capture strong correlation, unless one treats the system in a magnetically ordered phase. In this talk we illustrate some of these problems and efforts to go overcome them [1-3]. In particular, we focus on a many-body effective-energy theory (MEET) that gives many-body spectral functions in terms of reduced density matrices (RDMs) [4]. We show that simple approximations, which require the knowledge of the lowest n -body RDMs only, can provide accurate photoemission spectra in model systems in the weak as well as strong correlation regime. With the example of several transition metal oxides, we show that our method yields a qualitatively correct picture both in the antiferromagnetic and paramagnetic phases, contrary to mean-field methods, in which the paramagnet is a metal [4,5].

[1] P. Romaniello, F. Bechstedt, and L. Reining, *Phys. Rev. B* **85**, 155131 (2012).

[2] A. Stan, P. Romaniello, S. Rigamonti, L. Reining, and J.A. Berger, *New J. Phys.* **17**, 093045 (2015).

[3] Pierre-François Loos, P. Romaniello, and J. A. Berger, *J. Chem. Theory Comput.* **14**, 3071(2018); M. Véril, P. Romaniello, J. A. Berger, and Pierre-François Loos, *J. Chem. Theory Comput.* **14**, 5220 (2018).

[4] S. Di Sabatino, J.A. Berger, L. Reining, and P. Romaniello, *Phys. Rev. B* **94**, 155141 (2016).

[5] S. Di Sabatino, J.A. Berger, and P. Romaniello, arXiv:1903.09514

Electron-phonon coupling within quasiparticle self-consistent GW

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There is clear evidence that standard Density Functional Theory (DFT) underestimates electron-phonon coupling interaction in many materials, including even simple sp bonded compounds. Hybrid functionals and quasiparticle GW corrections suggest that nonlocal exchange-correlation enhances the electron-phonon interaction [1-5] as a consequence of an improved description of the electronic screening. This has highlighted the need to move beyond local exchange-correlation functionals within DFT, but complete *field-theoretic* investigations are still missing. In this talk I will introduce the development of a *field-theoretic* methodology which is able to predict on an equal footing electronic quasiparticles and phonons as well as their interaction. Such an approach has been implemented within the Quasiparticle Self-consistent GW (QS GW) formalism [6] which describes well the electronic properties for a wide range of materials [6], including many where standard DFT fails.

[1] J. L. Janssen, *et al.*, Phys. Rev. B **81**, 073106 (2010).

[2] Z. P. Yin, A. Kutepov, G. Kotliar, Phys. Rev. X **3**, 021011 (2013).

[3] A. Floris, S. de Gironcoli, E. K. U. Gross, M. Cococcioni, Phys. Rev. B **84**, 161102 (2011).

[4] M. Lazzeri, C. Attacalite, L. Wirtz, F. Mauri, Phys. Rev. B **78**, 081406 (2008).

[5] G. Antonious, S. Ponc  , P. Boulanger, M. Cot  , X. Gonze, Phys. Rev. Lett. **112**, 125501 (2014).

[6] T. Kotani, M. van Schilfgaarde, and S. V. Faleev, Phys. Rev. B **76**, 165106 (2007).

Beyond Kohn-Sham DFT: Explicitly correlated wave functions

Martin Panholzer¹

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In a recent study Medvedev et al. [1] showed that newly developed functionals in density functional theory (DFT), designed to improve in the energy estimate, do not necessarily reduce the error in the density, rather the opposite is seen. This, and the increasing number of specialized functionals, indicate the need of a paradigm change in DFT. We aim to improve the accuracy of ab initio methods by starting from a Jastrow correlated wave function, i.e. a product of the correlation factor F and a Slater-determinant ϕ_0 . The optimization problem splits in two coupled parts. First, the optimization of the correlation factor employs cluster expansion techniques. The Fermi-Hypernetted Chain (FHNC) summation technique is implemented to optimize the correlation function by energy minimization. Here even simple approximations [3] result, for the HEG, in more than 95 % of the exact correlation energy and yields a pair distribution function very close to Monte Carlo (MC) results for a wide density range. Within a manageable computational effort the method can be generalized to realistic periodic materials as demonstrated for a 1D model system [2]. The second part is the optimization of the orbitals of the Slater-determinant. This can be done in two different ways, i) a DFT like approach, where the exchange correlation potential V_{xc} is obtained from coupling constant integration of the exchange correlation hole and ii) from a generalized Hartree-Fock (gHF) equation, with different effective potentials in the exchange and direct part. The later is of particular interest, as it allows a direct interpretation of hybrid functionals. Preliminary results show a striking similarity of the exchange potential in e.g. HSE06 and the effective potential in the exchange part in gHF for the HEG. The final goal is to implement the coupled optimization of the correlation factor and the Slater-determinant for 3D materials as extension of present DFT implementations. We present the status of the development, in particular results for a periodic 1D model system [2] are shown. For a slowly varying density the local density approximation (LDA) is reproduced, but decreasing the period of the density variation, the results deviates from LDA, as expected. Finally an outlook on the performance for excited states is given.

[1] M. G. Medvedev et al., *Science* **355**, 49–52 (2017).

[2] M. Panholzer, *J. Low Temp. Phys.* **187**, 5–6 (2017).

[3] M. Panholzer, R. Hobbiger, and H. Böhm, *Phys. Rev. B* **99**, 195156 (2019).

Density fitting approach to many-body calculations in molecules and solids

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Density fitting is well established in quantum chemistry as a method for accelerating SCF and post-SCF calculations, including GW and BSE methods [1,2]. Here an all-electron, Gaussian orbital, Coulomb-metric density fitting method with applications to molecules and solids is reported. Calculation of Hartree-Fock exchange in solids is well known to present difficulties to numerical simulations owing to its divergent behaviour at small wave-vector. Local orbital basis approaches also suffer from the problem that contributions to the Fock operator do not converge when summed entirely in real-space. A Coulomb-metric density fitting approach to calculation of Hartree-Fock exchange or to Coulomb matrix elements over Bloch functions which appear in many-body methods leads to an Ewald summation in real and reciprocal space which is absolutely convergent. This is a feature of the factorisation introduced by density fitting. Performance of the density fitting methods with respect to auxiliary fitting basis, etc is analysed. The method is illustrated by time-dependent Hartree-Fock and GW/Bethe-Salpeter equation calculations on Na clusters [3] with up to 20 atoms and simple covalent solids using the Exciton code [4].

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Correlation and localization in reduced density-matrix functional theory

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Reduced density-matrix functional theory (RDMFT) allows for the description of systems with strong static correlation by using the fractionally occupied natural orbitals. As a result, localized electrons can be described via degenerate occupation numbers of orbitals which respect the symmetry of the system and are therefore delocalized. We study the relation between correlation and localization [1] for hydrogen chains of different lengths and compare the RDMFT results to those from Monte-Carlo simulations [2].

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Nonlinear optics from first-principles real-time approaches

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In the past decades, many-body approaches based on the GW approximation and the Bethe-Salpeter equation have become the state-of-the-art for calculating optical absorption in solids and nanostructures. In this talk, I'll first present a real-time approach derived from the non-equilibrium Green's function, that allows to extend the GW+BSE approach beyond the linear regime [1,2]. Using this approach, I'll address the importance of many-body effects and in particular of excitonic effects for nonlinear optical properties [3]. For example, I'll look at the case of single-layer monochalcogenide whose strong Second Harmonic Generation cannot be reproduced within the independent-particle approximation [4]. In the second part of the talk,

I'll then discuss the possibility of a real-time approach based on time-dependent density-functional theory, that can describe excitonic effects [5].

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Optical nonlinear processes in semiconductors in the presence of a DC field: An *ab-initio* description

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A deep understanding of the nonlinear optical properties of solids is crucial for the improvement of nonlinear devices and provides an opportunity to search for new materials. Among all the non-linear phenomena existing in nature, an important role is played by the electro-optic effect. The electro-optic effect produces a change of the refractive index in a medium using a DC electric field and has attracted particular interest for the development of optoelectronic devices. In the linear electro-optic effect (LEO) or Pockels effect, the change is proportional to the applied electric field. It may be seen as a second-order polarization and then described by a second-order susceptibility, which is known to be zero in the dipole approximation for centro-symmetric materials. Therefore a peculiarity of the LEO effect comes from the fact that it only occurs in materials without inversion symmetry or originates from symmetry-breaking regions.

From the theoretical point of view, most of the calculations for second-order susceptibilities have been done in the framework of Second Harmonic Generation (SHG), [1]. In that case, the frequency of the incoming field is considered as high with respect to vibrational frequencies and the lattice is kept static. Therefore, one has to evaluate only the electronic contribution, obtained directly from the optical susceptibility, coming from the interaction of the valence electrons and the electric fields. The knowledge of the electro-optic tensor implies in principle the evaluation of two additional contributions, the ionic and piezoelectric parts. The ionic contribution is linked to the ionic displacements and depends on the variation of the dielectric tensor induced by these displacements. The piezoelectric contribution comes from the possible modification of the shape of the unit cell due to the electric forces, [2]. Following the same idea, a similar phenomenon happens also for SHG, corresponding to a second harmonic response in the presence of a dc-field, called "Electric Field Induced Second Harmonic" (EFISH) and described in terms of a third-order polarization. I will show our results for the second order susceptibility describing the LEO tensor, within the *ab initio* framework of time-dependent density-functional theory. I will present our analytic derivation of the macroscopic polarization up to second order in terms of the electric fields, including the effect of a scissors operator to account for the quasi-particle effect. Excitonic effects will be included on the basis of a simple approach, [3]. The ionic contribution will be evaluated within the same framework and included explicitly. These results will be compared with experimental data. Furthermore, while the ionic part is often evaluated through the Faust-Henry coefficient [4], the validity of this approximation will also be discussed. Preliminary results will be presented for the EFISH process.

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Properties of electron-hole excitations: Screened exchange interaction and Q -resolved exciton band structure

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Optical experiments on nanostructures such as molecules, one- or two-dimensional materials, are often performed with the nanostructures in close proximity of a substrate or some other polarizable media. In this case, the Bethe-Salpeter Equation (BSE) can be used to calculate the optical excitations of the nanostructure by including the effect of the substrate via the screened electron-hole interaction [1]. Here we show, that in such an approach, where the states of the substrate are not explicitly included in the BSE Hamiltonian but only enter through the screened Coulomb interaction, it is important also to screen the electron-hole exchange interaction. For the case of molecules like benzene physisorbed on the metallic Au(111) surface, the screening of the exchange interaction by the substrate red shifts the lowest optical transition by up to 300 meV [2]. Furthermore, the screening of the exchange is essential in order to obtain the correct ordering of the size of quasi-particle and optical energy gap.

In the second part, we employ the $G W$ /BSE approximation to describe the entire Q -resolved exciton band structure for monolayers of the MX_2 ($M = \text{Mo, W}$ and $X = \text{Se, S}$) TMDCs [3]. We find that excitonic effects strongly influence the exciton band structure, i.e. strong electron-hole interactions are present throughout the entire Q -space. While the exciton binding energies of the lowest excitons do not vary significantly with Q , we find a strong variation in their coupling strength. Finally, we show that the Tamm-Dancoff approximation only marginally changes the results also for $Q \neq 0$.

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The connector theory: New approximations for the exchange-correlation potential

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In material science we often use model systems to describe real materials. In this talk we are interested in the question of how to import, in principle exactly, a quantity of interest from a model into a real system. The prescription how to do that is what we call "connector theory" [1]. An enormous advantage of this strategy is that model results can be obtained once forever and tabulated. After introducing the theory we will focus on approximating the exchange-correlation (xc) potential of density-functional theory (DFT) [2] including the time-dependent (TD) case, and we use the homogeneous electron gas (HEG) as the model system. Then we discuss the features of the connector theory and explain why it constitutes a better scheme for approximations than an approach that would directly approximate the xc potential. By making use of advanced calculations for the TDDFT xc kernel of the HEG [3], we derive xc potentials that have a non-local density dependence and are non-adiabatic. We consider some examples to discuss qualitative and quantitative differences between the results of our approach and those of the local-density approximation (LDA) and we show why our theory goes beyond the LDA. Finally we profit from the universal constraints on the exact xc potential as a guide to derive more accurate connectors, which yields better approximations to the xc potential.

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New approaches to TDDFT exchange-correlation kernels for theoretical spectroscopy

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We consider the description of the density-response function χ , part of which gives the optical absorption spectrum, with a focus on the prospects for improving the description of χ in time-dependent DFT. The key step in this process, the dynamic exchange-correlation kernel $f_{xc}(x, x', \omega)$, is studied by first calculating the exact response function χ for various interacting systems [1], and its counterpart for the auxiliary system of non-interacting electrons of exact Kohn-Sham DFT, χ_{KS} [2]. A new approximation for $f_{xc}(x, x', \omega)$ is presented [3], which, in total contrast to the adiabatic LDA, contains appropriate frequency-dependence (i.e. memory) and spatial non-locality.

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Inter-molecular charge-transfer states for organic opto-electronics

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Intermolecular charge transfer (CT) states at the interface between electron-donating and electron-accepting (A) materials in organic thin films are characterized by absorption and emission bands within the optical gap of the interfacing materials. Depending on the used donor and acceptor materials, CT states can be very emissive, or generate free carriers at high yield. The former can result in rather efficient organic light emitting diodes (OLED), via thermally activated delayed fluorescence, while the latter property is exploited in organic photovoltaic (OPV) devices and photodetectors. In this contribution, we will discuss the fundamental properties of CT states and link them to OLED and OPV device performance. We will discuss the influence of intra- and inter-molecular properties, such as the energy of the CT state, the electronic coupling between electron donor and acceptor, the molecular reorganization energy as well as non-radiative triplet states on radiative and non-radiative free carrier recombination. Furthermore, we introduce a new device concept, using an optical cavity resonance effect to boost CT absorption at photon energies below the optical gap of both donor and acceptor, enabling narrow-band, near infrared (NIR) photo-detection. Our findings imply that the power conversion efficiency of organic photovoltaics and maximum achievable detectivities for organic NIR detectors are limited by the presence of high energy vibrational modes and electron-phonon coupling.

Vibrations and their Impact on Absorption Spectra: Shaping Excitons in Organic Materials

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The low-energy edge of optical absorption spectra is critical for the performance of solar cells and lacks an in-depth understanding for organic materials. We have recently observed a strong dependence of low-energy absorption features on the organic material under study, which we associated to molecular flexibility and polaron deformation. Here, we develop an approach to simulate the excitonic density of states and low-energy absorption features including low-frequency molecular vibrations. This is applied to prototypical donor-acceptor blends featuring charge-transfer excitons. We study the temperature dependence of the absorption features in such systems and discuss the factors influencing their lineshape.

Optical response of layered hybrid lead halide perovskites: A complex interplay of dielectric confinement, electron-phonon coupling and point defects

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A sound understanding of the optical response of semiconducting materials is of paramount importance for the further improvement of photovoltaics and light emitting applications, currently representing strategic technologies for the future demand of green and abundant energy. In this sense, layered hybrid lead halide perovskites are a class of semiconductors that recently received huge attention for solar cell and light emission applications, thanks to their positive opto-electronic properties, along with low temperature synthesis and wide chemical tunability [1]. These compounds in fact are characterized by improved stability, compared to their 3D analogues [2], which however comes together with a more complex opto-electronic response, with spatial and dielectric confinement that results in formation of excitons characterized by sizable binding energy (around 300 meV) [3]. In this context, we performed a series of joint theoretical-experimental investigations aiming to disentangle the different phenomena influencing the complex absorption and emission properties of this class of hybrid semiconductors. Resonance impulsive stimulated Raman spectroscopy on two widely studied 2D perovskites (phenylammonium and buthylammonium lead iodide), show specific resonances associated to photoexcitation, in the frequency range below 50 cm⁻¹, which are well described in the context of electron-phonon interaction. Indeed, vibrational frequencies from DFT simulations well reproduce the experimental oscillations, providing a fingerprint of the lattice motion, with electron-phonon couplings falling in the range of 5-20 meV. Notably, related Huang-Rhys factors are comparable to those estimated in organic materials (few units), but with both relaxation energies and lattice motions lying on much smaller energy scale [4].

We further observed that the widely reported broadband emission at low temperature is consistent with the formation of emissive F-centers associated to the formation of halide-related interstitial defects, suggesting that the engineering of defects via chemical doping/substitution can represent a viable way to stabilize the broadband emission in a larger range of temperatures [5]. Altogether, the present contribution highlights the complexity of the opto-response of layered perovskites, where the quantum-well structure and associated excitonic properties come together with soft-lattice for these materials.

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Photoactive metal-organic frameworks for efficient gas separation

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Visible light was first shown in 2012 to act as an external stimulus for carbon capture-and-release in photoswitchable metal-organic frameworks (MOFs) [1]. Since then, this concept has attracted much attention because the use of light, rather than temperature, can potentially result in a more efficient mechanism, leading to a much cheaper technology, thus lowering the substantial cost of carbon capture and sequestration (CCS) processes. Recently, we demonstrated that in these MOFs [1,2] the notable change in gas uptake upon light irradiation is due to the blocking of the strongly adsorbing metal sites upon isomerization of the azo groups from *trans* to *cis* [3]. It follows that a large fraction of *cis* at the photostationary state would result in a higher efficiency. It is thus very important to design a MOF whose S_1/S_2 absorption bands are well separated between *trans* and *cis* so that the selective absorption of one isomer over the other would result in large fractions of each isomer at the photostationary state. In order to address this, we studied several azobenzene derivatives in solution and computed the optical absorption spectra using embedded GW/BSE calculations as implemented in FIESTA. Embedding at both DFT and GW/BSE level are found to be critical for an accurate description of selective absorption, together with an environment-consistent choice of the DFT xc functional. The change in optical properties from the ligand in solution to the MOF are studied and the choice of a fragment approach to study MOFs is discussed. CASSCF/CASPT2 and periodic GW/BSE are performed to benchmark, respectively, the DFT starting point and the choice of the fragment. Work supported by ANR-15-CE06-0003-01.

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Optical *in situ* spectroscopy of ultrathin organic films

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Optical spectroscopy is a powerful tool for probing physical processes and effects occurring in thin films of organic materials and at interfaces. A variant of absorption spectroscopy, the so-called differential reflectance spectroscopy (DRS) has been demonstrated to be especially suited for this task [1-2]. Beside the mere detection of excitonic properties of the films, which depend on the specific packing motif of the molecules, also electronic effects like charge transfer at interfaces or to/from dopants can be investigated in dependence of either the film thickness, starting from submonolayers, or the doping concentration. Recently, we enhanced the capabilities of our *in situ* optical setup even further by measuring the photoluminescence (PL) of the film quasi simultaneously. In my talk, I will discuss the advantages of having available both, light absorption and emission properties, for different film thicknesses on the example of the archetypical system perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on mica. It will be shown that only by the combination of both spectroscopies it could be elucidated that the treatment of the substrate prior to the film growth has a large impact on structural and electronic properties of the adsorbate. Such studies are anticipated to facilitate future theoretical studies in this field.

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A SiGe nanolaser, is it possible?

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Incorporation of microelectronics and optoelectronics is expected to revolutionize various fields of technology, such as communication, sensing, and imaging. A Si-based nanolaser would be the key to achieve integrated silicon photonics. However, Si as well as Ge in their diamond-structure equilibrium phases are known to be optically inactive due to the indirect nature of their band gaps. Since recently, the hexagonal allotropes of Si and Ge in the lonsdaleite phase can be grown in good quality. Hexagonal Si is still indirect, whereas hexagonal Ge is a direct semiconductor. Unfortunately, the dipole matrix elements of the lowest optical transitions are almost zero. Here, we show that it is possible to enhance the optical oscillator strengths of hexagonal Ge by applying tensile uniaxial strain or alloying it with Si. Upon structural modification, the two lowest conduction bands change order and the lowest optical transitions become strongly dipole active. We compare our results to recent data from our experimental collaborators. Using first-principles DFT calculations with hybrid functionals and the MBJLDA meta-GGA, we calculate structural and electronic properties and show how the absorption and emission spectra are affected by strain and alloying, respectively.

Non-invasive cross-sectional imaging of semiconductors with nanoscale resolution

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Optical coherence tomography (OCT) is an established method for non-invasive cross-sectional imaging of biological samples using visible and near infrared light. The axial resolution of OCT only depends on the coherence length $l_c = \lambda_0^2 / \lambda_{\text{FWHM}}$, with the central wavelength λ_0 and the spectral width λ_{FWHM} of the light source. Here, the axial resolution is in the range of a few micrometers. XUV coherence tomography (XCT) extends OCT into the extreme ultraviolet and soft x-ray range. The significant reduction of the coherence length of a broadband XUV source allows nanoscale axial resolution. The usable spectral bandwidth in XCT is mainly limited by absorption edges of the sample under investigation. For example, the so-called silicon transmission window allows cross-sectional imaging of silicon-based circuits.

A laboratory-based XCT setup has been implemented by using XUV radiation from a laser-driven high harmonic source. By averaging harmonic combs generated by different fundamental wavelengths, a quasi-supercontinuous spectrum, which is well-suited for XCT, is generated. The radiation is focused onto the sample and the reflected radiation is recorded. Interferences due to reflections at structures in different depths result in modulations in the measured spectra that can be used to reconstruct the axial (i.e. depth) structure of the sample.

Experimentally we achieve an axial resolution of 24 nm.

Challenges and potentials: Experiences from super-resolution microscopy in biomedical research

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Understanding the complex interactions of molecular processes underlying the efficient functioning of the human body is one of the main objectives of biomedical research.

Scientifically, it is important that the applied observation methods do not influence the biological system during observation. A suitable tool that can cover all of this is optical far-field fluorescence microscopy and spectroscopy. Yet, biomedical applications often demand coverage of a large range of spatial and temporal scales, and/or long acquisition times, which can so far not all be covered by a single microscope and puts some challenges on microscope infrastructure. Taking immune cell responses and plasma membrane organization as examples, we outline these challenges but also give new insights into possible solutions and the potentials of these advanced microscopy techniques, e.g. for solving long-standing questions such as of lipid membrane rafts.

Time resolved electrons dynamics in layered semiconductors

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We investigate black phosphorus by time- and angle-resolved photoelectron spectroscopy. The electrons excited by 1.57 eV photons relax down to a conduction band minimum within 1 ps. In the thermalized state, the band gap renormalization is negligible up to a photoexcitation density that fills the conduction band by 150 meV. Astonishingly, a Stark broadening of the valence band takes place at an early delay time. We argue that electrons and holes with a high excess energy lead to inhomogeneous screening of near surface fields. As a consequence, the chemical potential is no longer pinned in a narrow impurity band. In the second part of the talk I will discuss hot carriers cooling in a two dimensional electron gas on InSe. We show that the cooling rate can be correctly reproduced by first principle calculations accounting for the Pauli blocking of intraband transitions and many-body screening of the Froehlich coupling.

Attosecond spectroscopy of crystals: Wigner delay, Hartman effect, and external fields

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The talk is devoted to band structure aspects of the attosecond streaking experiment [1], i.e., how the interaction of the outgoing photoelectron with the crystal lattice affects its propagation and dynamics. The effect of the lattice scattering at short travel times is analyzed using a microscopic one-dimensional model of the streaking experiment as well as by *ab initio* calculations for graphene and graphite. By numerically exactly solving the non-stationary Schrödinger equation for laser-assisted photoemission we reveal the crucial role of the exciting field in electron propagation: when the optical pumping is accompanied by a strong lattice scattering the wave packet may move faster than with the group velocity [2]. Furthermore, the quantum nature of the photoelectron is important when it is accelerated by a laser field inside the crystal: the band structure effects may lead to a shift of the streaking spectrogram not related to electron transport [3].

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Photoelectron momentum maps (PMMs): A tool to investigate molecular properties

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About ten years ago, a new method called photoelectron momentum maps (PMMs) became available, which has proven to be extremely useful for the study of ultra-thin films of organic molecules on single crystalline surfaces. This is based on the observation that the intensity distribution of the photoelectrons in k -space at a constant binding energy is approximately proportional to the Fourier transform of the respective molecular orbital. In this talk, we want to describe the working principles of this method covering on the one hand the experimental requirements to measure PMMs. On the other hand, we will discuss the theoretical approaches to simulate them, which is highly important to understand the results unambiguously. Recent examples concerning polycyclic aromatic hydrocarbons on noble metal surfaces will highlight the advantages as well as the drawbacks in the investigation of photoelectron angular distributions.

***Ab initio* description of pump and probe experiments: From carriers to exciton dynamics**

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The Kadanoff-Baym equation reduces to an equation of motion for the one-body density matrix within the Generalized Kadanoff Baym ansatz. Moreover, introducing a Markovian and a Boltzmann like approximation for the collision integral, its *ab-initio* implementation becomes feasible also for extended systems [1-3]. Indeed we have shown it well describes carriers dynamics, lifetimes and transient spectroscopy in bulk silicon[4-6]. The interpretation of the physics captured is straightforward, in terms of coherent and the non-coherent dynamics of electrons and holes, in particular if the static part of the self-energy is kept at equilibrium. Correlation however need to be switched on to describe renormalization effects, coherent processes and decoherence, the absorption of light at exciton resonances [1] and the physics of non-coherent excitons [7-8]. It becomes then non trivial to give a simple physical interpretation to the resulting equations. Starting from carriers dynamics I'll discuss how such different physical aspects can be tackled within the non-equilibrium Green's function formalism, still connecting the equations to clear physical concepts. I'll focus in particular into the concept of exciton dynamics and exciton lifetimes [8].

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Exciton temperature dependence dictated by localisation in organic semiconductors

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The optoelectronic response of organic semiconductors in technological devices is dominated by room temperature excitons. However, excitonic calculations of organic crystals at finite temperature can be very challenging, due to the need to combine the effects of exciton-phonon coupling and thermal expansion. Here we overcome this challenge by employing a combination of Green's function methods for the electronic structure, and non-perturbative finite difference methods for the interaction with the lattice, in archetypal organic semiconductor pentacene. We find that the different localization ranges of exciton singlet and triplet states lead to distinct responses to both exciton-phonon coupling and thermal expansion. Independently, these two effects strongly drive the temperature dependence of exciton energies, but their opposite sign leads to a combined temperature dependence that is overall weak, qualitatively reproducing the experimentally measured blue shift of the singlet level with increasing temperature. We expect that the combination of exciton-phonon coupling and thermal expansion, together with their interplay with the exciton localization range, provides a general mechanism for understanding the temperature dependence of exciton energies in molecular crystals.

***Ab Initio* Exciton Dynamics and Radiative Recombination**

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Excitons are bound electron-hole pairs that dominate the optical response of semiconductors and insulators, especially in materials where the Coulomb interaction is weakly screened. Light absorption (including excitonic effects) has been studied extensively using first-principles calculations, but *ab initio* methods for computing radiative recombination and light emission are still being developed. Here we show a unified *ab initio* approach to compute exciton radiative recombination in materials ranging from bulk crystals to nanostructures and molecules. We derive the rate of exciton radiative recombination in bulk crystals, isolated systems, and in one- and two-dimensional materials, using Fermi's golden rule within the Bethe-Salpeter equation (BSE) approach. We present calculations of radiative lifetimes in systems ranging from two-dimensional transition metal dichalcogenides (TMDs) to a GaN crystal and organic molecules. In TMDs, our calculations show that light emission can be anisotropic in spite of their in-plane isotropic atomic structure, and in GaN and in organic molecules our computed radiative lifetimes are within a factor of 2 of experiment, without using any empirical or fitting parameters. The talk will additionally discuss our efforts toward computing the ultrafast dynamics of excitons in real time. We first derive a framework for computing exciton-phonon interactions from first-principles within the BSE approach, and then we apply it to compute exciton-phonon coupling and relaxation times in hexagonal boron nitride. We will close by discussing how this approach can be extended to time-step the exciton occupation in momentum space within the *ab initio* Boltzmann transport equation framework.

Code development efforts, open problems and future directions will also be outlined.

Interaction of intense laser fields with matter

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The recent progress in the development of ultrashort, intense laser pulses and their interaction with matter paved the way to new interesting phenomena, both for fundamental research and for applications. As examples, short, intensive laser pulses are commonly employed in (eye) surgery or material processing. In fundamental research, processes such as the generation of higher order harmonic radiation, leading to the generation of ultrashort, attosecond pulses are subject of investigation. In this talk, I will provide an overview over the interaction of intense laser pulses with matter. Starting from a general introduction into strong-field physics, I will present examples of our work: I will show why molecules fragment or not, depending on their relative orientation to the laser polarization axis [1,2] and demonstrate how such processes can be measured or visualized, e.g. by laser-induced electron diffraction [3,4].

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Dielectric function of homogeneous electron gas from Bethe-Salpeter equation

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The homogeneous electron gas (HEG) is one of the most important model systems in condensed matter physics, and it has been subject of a great number of studies. Some properties of the HEG such as total energy and static correlation functions can be obtained from quantum Monte Carlo (QMC) simulations with great accuracy, but for dynamical correlation functions only very few results are available. Methods based on the Bethe-Salpeter equation (BSE) have been very successful in semiconductors and insulators, but metals have been less studied. In this contribution, we use the BSE in its standard approximations, including a statically screened electron-hole interaction, to study the dielectric function of the

HEG. We find significant differences in static screening and spectra compared to other approaches. In particular, the BSE in its current approximations fails to reproduce the negative static screening in the low-density HEG, which is related to a so-called ghost exciton [1,2]. We discuss the possible reasons for this shortcoming, and potential directions for improvement.

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Optical properties in thin layer materials

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In the framework of periodic boundary codes, the standard way to describe surfaces, or more generally isolated objects, is to build a supercell with vacuum, to separate the artificial replicas.

We have shown in the recent past that this procedure gives an absorption spectrum which depends on the vacuum introduced in the supercell [1]. In the surface case, this effect is particularly dramatic for the out-of-plane component, when the local field effects are taken into account. We have proposed a new method called Selected-G to solve this vacuum problem. In TDDFT, it consists to solve the Dyson equation on a reduced set of reciprocal lattice vectors defined according to the thickness of the matter, and not related to the supercell.

During the derivation of this method, we have evidenced a non-diagonal expression for the Fourier transform of the Coulomb potential, called slab potential [1]. In the limit of an infinite thickness of matter, we recover the standard 3D expression of the Coulomb potential, and the Selected-G procedure has been successfully applied to describe absorption [1], and second harmonic generation for silicon surfaces [2]. The full expression of the slab potential allows the comparison between the slab and surface absorption spectra. In the case of electron energy loss (EEL) spectra, the vacuum problem also affects the in-plane components and one must use the full expression of the slab potential in the Selected-G formalism to reproduce experimental spectra [3], as it will be illustrated for few layers graphene slabs. These results open the question of the relationship between EEL and absorption spectra for thin slabs of matter.

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Electron-Magnon Scattering from First Principles within the GT and GWT Self-Energies

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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. To this end, a \mathbf{k} -dependent self-energy (GT self-energy) describing the scattering of electrons and magnons is constructed from the solution of a Bethe-Salpeter equation for the two-particle (electron-hole) Green function, in which single-particle Stoner and collective spin-wave excitations (magnons) are treated on the same footing. Partial self-consistency is achieved by the alignment of the chemical potentials. The resulting renormalized electronic band structures exhibit strong spin-dependent lifetime effects close to the Fermi energy, which are strongest in Fe. The renormalization can give rise to a loss of quasiparticle character close to the Fermi energy, which we attribute to electron scattering with spatially extended spin waves. This scattering is also responsible for dispersion anomalies in conduction bands of iron and for the formation of satellite bands in nickel. 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. First results of a combination of the GT self-energy with GW (GWT) are presented. We also discuss a possible violation of causality when an incomplete subset of self-energy diagrams is chosen.

XAS as a powerful tool for rationalizing electrochemical processes in Li/Na-ion batteries

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Lithium-ion batteries are nowadays primary energy source for portable electronics and are of great importance for electric transportation. They operate on cationic redox reactions accompanied by insertion-deinsertion of Li (during discharging and charging respectively). To meet increasing market requirements, improvement of batteries parameters, in particular the energy density, is an ongoing research in the field of electrochemical energy storage. Recently it was shown that Li-rich layered transition metal oxides (LLTMOs), used as a positive electrode, are promising for increasing energy density of Li and Na ion batteries [1-3]. These systems consist of alternating lithium and transition-metal layers where metal (M) in the metallic layer is partially substituted by Li, which enables a cumulative cationic (M^{4+}/M^{5+}) and anionic ($2O^{2-}/(O_2)^{n-}$) redox activity, thus increasing the energy density. The O-network oxidation was proposed to be associated with the formation of short O-O bonds (~ 2.4 Å with respect to initial 2.7 Å). However, the oxidation of oxygen can lead to irreversible structural transformations, voltage hysteresis or even oxygen release, which preclude LLTMO-cathodes from commercialization. Recent theoretical results suggest that the electronic ground state of the lithiated oxides (Mott-Hubbard or charge transfer) and the amount of holes generated on the O-network are the key parameters for reversible anionic redox to occur [4]. In our work, we want to answer whether the X-ray absorption spectroscopy (XAS) can be a technique of choice to follow structural and electronic changes in LLTMOs while charging/discharging. We are focusing here on Li_2IrO_3 system where the question of either pure cationic or mixed cationic and anionic redox is still under the debate. During the cycling process Li^+ ions can be extracted either from the transition-metal layer or from the lithium layer and various delithiated configurations have to be considered. Consequently distinct $Li_{2-x}IrO_3$ ($0 \leq x \leq 2$) structures were created and then relaxed using density functional theory (DFT) as implemented in the VASP [5] code within the projector augmented wave (PAW) method. The exchange-correlation functional was calculated within generalized gradient approximation (GGA) and its GGA+U variant to improve description of electronic structure of strongly correlated materials. Next, we calculated oxygen K-edge for obtained $Li_{2-x}IrO_3$ structures with different electronic ground states and we followed the K-edge evolution at various delithiation stages. XAS was evaluated within widely used FDMNES [6] code that implements both the finite difference method and multiple-scattering approach to calculate absorption spectra for a given atomic species. We show that by choosing finite difference approach with more accurate description of the potential the resulting theoretical spectra are in good agreement with experimental data. Moreover, through deep analysis of various structural models we were able to confirm the electrochemical mechanism described in Ref. [4], i.e. a mixed cationic and anionic redox.

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X-ray absorption spectroscopy of semiconductor alloys

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Semiconductor alloys are widely used for electronic, optoelectronic and photovoltaic devices

because their material properties can be specifically tailored by adjusting the material composition. $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ is used as absorber layer in thin film solar cells with a record efficiencies of more than 23%. However, alloying often introduces a discrepancy between element-specific short-range properties and average long-range properties. The talk will

demonstrate how X-ray absorption spectroscopy (XAS) can be applied to study

element-specific local structural and electronic properties of semiconductor alloys as a function of composition. Bond lengths, atomic displacements and their impact on the band gap energy will be discussed for $\text{Cu}(\text{In,Ga})\text{Se}_2$ and $\text{Cu}(\text{In,Ga})\text{S}_2$ including both experimental XAS results and theoretical predictions. Furthermore, the local electronic states comprising the conduction band of the material are investigated, again, by combining experimental XAS with ab initio calculations.

Unraveling the oxidation state of manganese corroles on Ag(111)

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Corroles are tetrapyrrole macrocycles with promising applications in various fields of science, e.g., chemistry, bioscience, medicine and solar cells applications. Their peculiarity of stabilising

high valent metal states promote oxidation reactions and makes this class of molecules interesting for catalytic applications. However, despite being crucial for their functionality, the electronic structure of corroles is often hardly accessible with traditional techniques especially

under interfacial conditions. Here, we present a multi-technique strategy based on density functional theory (DFT) calculations, element-specific X-ray spectroscopy techniques and in situ atomic force microscopy (AFM) to unravel the electronic ground structures and the

oxidation states of the prototypical Mn-5,10,15-tris(pentafluorophenyl)corrole complexes as well as of their thermally induced derivatives adsorbed on Ag(111). Our results, in particular the theory-assisted interpretation of Mn photoemission and absorption fine structure spectra, show that Mn centres prevail the bulk characters despite the contact to the metal surface.

Furthermore, they enable a comprehensive understanding and a deep insight into the on-surface chemistry of such complex molecular systems on the atomic-scale level.

QED-Bloch Theory with Homogeneous Magnetic Fields: Modifications of the Landau Levels and the Hofstadter Butterfly

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Probing electronic properties of periodic systems by arbitrary homogeneous magnetic fields has unravelled fundamental new phenomena in condensed matter physics. Much theoretical work has been devoted to describe those systems in different regimes, still a general first principles modeling of such fundamental effects is lacking. Here we propose a solution to the problem of Bloch electrons in a homogeneous magnetic field by including the quantum fluctuations of the photon field. A generalized quantum electrodynamical (QED) Bloch theory from first principles is presented. As an application we show how the well known Landau physics is modified by the photon field and that Landau polaritons emerge. Moreover, in the case of a 2D solid in a perpendicular magnetic field, in the limit where the field fluctuations go to zero, we recover the fractal pattern of the Hofstadter butterfly. Further generalizations and modifications of the Hofstadter butterfly will be presented.

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All-electron many-body perturbation theory for core spectroscopy in organic, inorganic, and hybrid materials

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First-principles methods based on density-functional theory and many-body perturbation theory are state-of-the-art approaches to study light-matter interaction in solid-state materials. Their implementation in all-electron schemes, such as the one provided by the `exciting` code [1], offers the additional opportunity to calculate core excitations on the same footing as the optical ones [2,3]. After introducing the underlying methodology, I will demonstrate the predictive power of our approach for computing X-ray absorption spectra and excitations with a few recent examples on different material classes, ranging from bulk crystals [2,4,5] to organic semiconductors [6] and hybrid inorganic-organic perovskites [7]. I will address the role of spin-orbit coupling and discuss how correlation effects impact core excitations depending on the nature of the material as well as on the excited edge.

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***Ab initio* calculation of the band-gap of liquid water: Insight from spectroscopy**

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We present *ab-initio* optical and Inelastic X-ray Scattering spectra (IXS) of liquid water calculated within the frameworks of the Bethe Salpeter Equation (BSE) and Time Dependent Density Functional Theory (TDDFT). From the extensive comparison of our theoretical results with available experimental data we are able to extract information concerning the electron screening. We employ this new insight to reduce the ambiguities in the liquid water theoretical band-gap value.

Electron-Hole Correlation in Resonant Inelastic X-ray Scattering of Solids

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In this talk, I will present a novel many-body approach to resonant inelastic x-ray scattering (RIXS). This approach makes use of excited states both in the optical and x-ray region, obtained from full diagonalization of the Bethe-Salpeter equation. In order to describe core and valence excitations consistently, we employ an implementation of the many-body perturbation theory

in an all-electron framework in the `exciting` code. I will show how to reformulate the Kramers-Heisenberg formula in terms of pathways between excited core and valence states in a many-body picture. These excitation pathways allow for an intuitive interpretation of the electron-hole correlation in the RIXS process. Our formalism furthermore yields an explicit expression for both coherent and incoherent contributions to the RIXS cross section. I will show the application of this in-depth analysis to the RIXS spectra of two prototypical systems, namely the F K edge of LiF and the C K edge of diamond. I will demonstrate that a careful treatment of electron-hole correlation is crucial for an accurate description of the RIXS process.

Poster contributions

Deviation of Rydberg Excitons from Hydrogenic Series in Semiconductors: Is Nonparabolicity All That Matters?

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We often rely on one or few parameters when trying to turn experimental measurements into a comprehensive picture, and sometimes we might forget that a better instrument or a bigger computer will not reduce the error bars because the original model itself was an approximation. In this work we concentrate on Rydberg exciton series in absorption spectra of semiconductors and take a closer look at two parameters used by Elliott's model: reduced mass μ and dielectric constant ϵ_0 which enter the equation for exciton binding energy as $E_B \mu/\epsilon_0^2$. The deviation of theoretical results from experimental measurements are usually blamed on nonparabolicity effects of the effective mass. Here we introduce a method which yields a different dielectric constant for each excitonic resonance. This allows us to correct for overscreening in Elliott's model because the excitons with lower quantum number are less delocalized in space and thus experience less dielectric screening by the phonons. We apply our model to a set of 18 direct band gap semiconductors for which we calculate exciton binding energies, dielectric constants, and reduced masses. Knowing E_B , dielectric constant and effective electron mass from experiment, we compute reduced effective masses from which we infer the effective hole masses and compare them to the available experimental measurements and density functional theory calculations. We show that the validity of Rydberg exciton theory may be extended to higher energies without the need of fitting parameters such as those of quantum defect theories. Also, by analyzing the large volume of theoretical and experimental data, we are able to turn this problem into an inverse materials design problem, namely using the data to test the validity of a commonly used theoretical model.

Nonlinear electronic transport behavior of γ -graphyne nanotubes

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In this work, we have investigated the electronic transport properties and current-voltage characteristics of the armchair and zigzag γ -graphyne nanotubes by the SIESTA and TRANSIESTA packages including density functional theory and non-equilibrium Green's function for the four chiral vectors 2, 3, 4 and 5. We found that the current in γ -graphyne nanotubes is very negligible for low bias voltages, but it enhances precipitously for voltages above the threshold voltage. Both zigzag and armchair γ -graphyne nanotubes reveal negative differential resistance, for specific diameters, which is a promising result for nano-based device usages like switching and memory circuits. Finally, the characteristics of these nanotubes are similar to those of a two-way tunneling diode. Therefore, we can expect a new application that produces oscillation.

Time-resolved cavity ring-down spectroscopy

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The aim of this project is to build and characterize a spectroscopic system called cavity ring down spectroscopy (CRDS) and combine it with femtosecond pump-probe spectroscopy. In this manner, we intend to temporally resolve the transient absorption of thin films by measuring the decay of excited states with a lifetime as short as few tens of femtoseconds. CRDS is reported to be an excellent approach to measure low absorbing gas phase samples, like traces of gases at atmospheric pressure, achieving in general a resolution of 2-3 orders of magnitude higher than conventional absorption spectroscopy. Recently, many publications have proven a successful adaptation of CRDS to investigate liquid phase samples. However, not many reports have been yet dedicated to measure the absorption of thin films or monomolecular layers and specifically, there is no reported research about time-resolved CRDS on two-dimensional condensed samples. The current interest on the fabrication of such structures like carbon nanomebranes, Langmuir-Blodget films or any kind of ultrathin functional interfaces, requires a facility that is able to explore their interaction with light and their photoactivated charge transfer processes.

Combining Local-Density Approximation and the GW Method

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We present a theoretical framework which combines density functional theory with Green's function. The framework separates electron-electron interactions into two components: short and long ranges. For short range contribution, density functional theory provides exchange-correlation potential, while Green's function calculates self-energy for the long range. The framework is called Chachiyo-GW which combines local-density approximation and the GW method.

Hydrogen adsorption on Na and Li decorated WTe₂

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In this paper, we investigate the effect of adsorption of hydrogen on the surface of the WTe₂ that decorated with Na and Li. The first principle calculations based on the density functional theory showed that due to the larger energy of the sodium and lithium atoms on the WTe₂ surface relative to the cohesive energy of these atoms in bulk, Li and Na atoms can be as a single atom on the surface of the WTe₂ not as clusters atoms. By decoration of WTe₂ with Na and Li atoms the structures can be behavior as metal. By absorbing hydrogen molecules on the surface of WTe₂, the results show that the Li atom was able to absorb more hydrogen molecules and could be used as a promising candidate in the storage field as well as the hydrogen gas sensor.

Electronic properties of fluorides by efficient approximated quasiparticle DFT-1/2 and PSIC methods: CaF_2 , BaF_2 and CdF_2 as test cases

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Dialkali halides are materials of great interest from both fundamental and technological viewpoint, due to their wide transparency range. The accurate determination of their electronic (ground and excited state) and optical properties in bulk and low dimensional structures is therefore of crucial importance nowadays. Here we report electronic quasiparticle band structures for three representative bulk fluorides, CaF_2 , BaF_2 and CdF_2 , calculated using two methods, the DFT-1/2 and the PSIC schemes, which have been relatively poorly explored by the theoretical community, so far. Our results, compared with both available experimental data and previous DFT-GW self-energy calculations, demonstrate a satisfying accuracy for the examined compounds, at a level comparable with the perturbative G_0W_0 approach.

Remarkably, both our proposed methods scale quite similarly to standard local density functional approaches, thus resulting in a large saving of computational effort with respect to the computationally more demanding GW schemes. Our results opens up the perspective of the computational exploration of much challenging fluoride systems. As a significant proof of concept of this capability, we also calculated by the DFT-1/2 and PSIC schemes the quasiparticle properties of the (111) surfaces of all the three systems under study.

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Quantum-classical molecular dynamics in the canonical ensemble

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We derive the canonical ensemble of hybrid systems (i.e. those that combine both classical and quantum particles) from the principle of maximization of entropy. For that purpose, one must properly define the entropy of hybrid systems. This canonical ensemble distribution is not preserved under Ehrenfest dynamics, as we numerically prove with a model system. The fact that Ehrenfest dynamics, in combination with a common thermostat, does not properly equilibrate to the right equilibrium populations had been observed previously, but those computations did not prove the non-stationarity of the canonical ensemble, as we discuss here: Ehrenfest systems, just as purely classical or quantum ones, can be viewed as classical Hamiltonian systems, and therefore the classical Gibbs ensemble is *also* stationary – although is not the real equilibrium one, as it does not not maximize the correct entropy. Unfortunately, the calculation of ensemble averages via the standard Molecular Dynamics procedure of attaching a typical thermostat (Nosé-Hoover, Langevin's) and averaging over ergodic trajectories implicitly assumes this wrong ensemble, and in consequence leads to wrong averages. This is not a defect of Ehrenfest dynamics, but a consequence of the application of methods designed for purely classical systems to hybrid ones. Finally, we provide some formulas that permit to compute the correct canonical ensemble averages from thermostatted Ehrenfest dynamics, thanks to a modified time-averaging procedure.

Electronic Structure, Electron-Phonon Coupling, and Charge Transport in Crystalline Rubrene Under Mechanical Strain

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Motivated by the potential for application of organic semiconductors in flexible electronics, we present a theoretical study aiming at elucidating the interplay between mechanical strain and electronic, vibrational and charge transport properties of the prototypical high-mobility molecular semiconductor rubrene [1].

Our study considers several factors that can play a role in the electro-mechanical response of a soft, van-der-Waals bonded, molecular crystal, such as intermolecular charge transfer integrals, lattice dynamics and electron phonon coupling. We find that compressive strain leads to an increase in magnitude of charge transfer integrals but also of the energetic disorder hampering the mobility. Charge transport simulations, based on the transient localization framework [2] and fed with first-principles inputs, reveal a remarkably different response to strain applied along different crystal axes, in line with most recent experiments. The critical interplay between energetic disorder of intrinsic and extrinsic nature on the mobility-strain relationship is also discussed. The theoretical approach proposed in this work paves the way for the systematic study of the electro-mechanical response of different classes of high-mobility molecular semiconductors.

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First principles prediction of the solar cell efficiency of chalcopyrite materials AgMX_2 ($\text{M} = \text{In, Al}$; $\text{X} = \text{S, Se, Te}$)

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Using the Spectroscopic Limited Maximum Efficiency, and Shockley and Queisser predictor models, we compute the solar efficiency of the chalcopyrites AgMX_2 ($\text{M} = \text{In, Al}$; $\text{X} = \text{S, Se, Te}$). The results presented are based on the estimation of the electronic and optical properties obtained from first principles density functional theory as well as the many-body perturbation theory calculations. The results of this report were consistent with the experimental data. The optical bandgap was accurately estimated from the absorption spectra, obtained by solving the Bethe and Salpeter equation. Fitting the Tauc's plot on the absorption spectra, we also predicted that the materials studied have a direct allowed optical transition. The theoretical estimations of the solar cell performance showed that the efficiencies from the Shockley and Queisser model are higher than those from the spectroscopic limited maximum efficiency model. This improvement is attributed to the absorption, the recombination processes and the optical transition accounted in the calculation of the efficiency.

Coverage-dependent anisotropy of the NTCDA/Ag(111) interface state dispersion

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The adsorption of π -conjugated organic molecules on metallic substrates often produces peculiar electronic structures that result from interactions between energetically discrete and localized molecular orbitals on the one hand and continuous and delocalized states of the metal on the other. The two-dimensional, highly dispersive interface states (IS) that appear at such interfaces are particularly noteworthy. We employ density-functional theory (DFT) to analyze the dispersion of the IS between a monolayer of 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride (NTCDA) and the Ag(111) surface. We present and verify a hydrogen termination approach which allows a meaningful DFT description of the IS with relatively thin silver slabs. Complemented with a projection technique which maps the interface electronic structure onto the original Ag(111) Shockley state, the DFT calculations enable us to analyze the evolution of the dispersion of the NTCDA/Ag(111) IS when changing of the molecular coverage. Additionally, we perform Fourier transform (FT) scanning tunneling spectroscopy (STS) experiments on a relaxed phase NTCDA/Ag(111) monolayer. Our calculations predict a pronounced anisotropy of the dispersion of the IS at long wavelengths which depends linearly on the molecular coverage. The dispersion anisotropy is fully confirmed by our FT-STs experiments.

SUNRISE – Solar energy for a circular economy

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The SUNRISE project is one out of six Coordination and Support Actions (CSA) recently selected by the European Commission to establish a large-scale European research initiative. Currently, the production of fuels and base chemicals is very energy intensive and requires a large amount of fossil resources. SUNRISE aims to develop a sustainable alternative to these traditional processes. The proposed approach uses the energy provided by the sun and exploits raw materials abundantly available in the atmosphere: carbon dioxide (CO₂), oxygen and nitrogen. In the short term, renewable electricity sources and waste CO₂ from industrial processes represent the necessary input for the sustainable production of fuels and chemicals.

In the long term, sunlight provides directly the energy to convert molecules from the atmosphere using radically new approaches (e.g. of photochemical or biological nature). Within the framework of the CSA, SUNRISE benefits from a financing of 1 million euros during one year, intended to develop a technological roadmap, to mobilize partners and to establish an efficient system of governance. UCLouvain is responsible for the coordination of the Belgian network and the establishment of the technological roadmap. SUNRISE has so far received the support of more than 200 actors from research, industry and the public sector. This contribution will provide details about the project's vision and mission, its partners and supporters and will serve as gathering point for those interested in reinforcing the SUNRISE community.

Reduction of rank in the dielectric function of semiconductors

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Organic semi conductors have molecules with many atoms atoms in their unit cell. Hedin's GW approximation predicts their gaps with reasonable accuracy, but the construction of their dielectric functions remains a computational bottleneck. To address this difficulty, we show that the dielectric function of semiconductors can be constructed in sub spaces of reduced dimensions, while keeping $O(N^3)$ scaling.

Identification of sp^1 Hybridized C in Surface-Grown Molecular Assemblies by Core-Level Spectroscopy

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The advent of on-surface chemistry and molecular self-assembly opened the way to the realization of organic materials whose lack of stability in vacuo would otherwise forbid their synthesis. Recently the on-surface coupling of the precursors have also been used to synthesize adsorbed organic systems with chemically vulnerable linear carbon chains with sp^1 hybridization [1]. A notable advantage of on-surface synthesis is that the full realm of the experimental and theoretical surface science toolbox is available for the investigation. While the method of choice for surface-supported architectures is the scanning tunneling microscope and ultimate resolution is achieved by low-T non-contact atomic force microscopy, electron core-level spectroscopy can provide an even more local probe of the electronic properties of the material. In particular, polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is here suggested to discriminate sp^1/sp^2 character in the structures. We present an ab initio study of the polarized NEXAFS spectrum of model and real sp^1/sp^2 materials. Calculations are performed within density functional theory with plane waves and pseudopotentials, and spectra are computed by core-excited C potentials as validated by previous studies [2,3]. We evaluate the dichroism in the spectrum for ideal carbynes and highlight the main differences relative to typical sp^2 systems. We then consider a mixed polymer alternating sp^1 C_4 units with sp^2 biphenyl groups, recently synthesized on Au(111) [4], as well as other linear structures and two-dimensional networks, pointing out a spectral line shape specifically due to the presence of linear C chains [5]. Our study suggests that the measurements of polarized NEXAFS spectra could be used to distinctly fingerprint the presence of sp^1 hybridization in surface-grown C structures.

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Influence of anisotropy, tilt and pairing of Weyl nodes: The Weyl semimetals TaAs, TaP, NbAs, and NbP

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By means of *ab initio* band structure methods and model Hamiltonians we investigate the electronic, spin and topological properties of four monpnictides crystallizing in body centered tetragonal structure. We show that the Weyl bands around a Weyl point W1 or W2 possess a strong anisotropy and tilt of the accompanying Dirac cones. These effects are larger for W2 nodes than for W1 ones. The node tilts and positions in energy space significantly influence the density of states of single-particle Weyl excitations. The node anisotropies destroy the conventional picture of (anti)parallel spin and wave vector of a Weyl fermion. This also holds for the Berry curvature around a node, while the monopole charges are independent as integrated quantities. The pairing of the nodes strongly modify the spin texture and the Berry curvature for wave vectors in between the two nodes. Spin components may change their orientation. Integrals over planes perpendicular to the connection line yield finite Zak phases and winding numbers for planes between the two nodes, thereby indicating the topological character.

Electronic and optical properties of two-dimensional magnets: CrI_3 and $\text{WSe}_2/\text{CrI}_3$

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For the development of novel opto-electronic devices the access and in particular the manipulation of the spin degree of freedom is of fundamental importance. In recent years two-dimensional (2D) materials have come to the fore owing many unique properties. A profound understanding of the delicate interplay of spin, orbital, charge and lattice degree of freedom in these materials is essential for further development. Recently the chromium trihalide CrI_3 has attracted significant attention as it shows a ferromagnetic behaviour down to the monolayer limit.

In this poster we first discuss the results of our ab-initio calculations of monolayer CrI_3 . We investigated the structural properties on the basis of DFT(LDA) which provides a good starting point for the many body perturbation theory (MBPT). Within the LDA+ GdW approximation we study the electronic and magnetic properties and find a gap of 2.283 eV. By solving the Bethe-Salpeter equation we evaluate the optical absorption and find a large exciton binding energy of 1.06 eV.

In the second part we build a heterostructure from monolayer CrI_3 and the well studied semiconducting transition metal dichalcogenide (TMDC) tungsten diselenide (WSe_2). By combining these two materials we find that the energy degeneracy of the spin-split valence and conduction bands of WSe_2 at K^\pm is lifted due to the proximity effect with the underlying ferromagnetic monolayer.

Coherent phonon dynamics traced by high harmonic generation in ZnO

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Ultrafast coherent phonon dynamics in ZnO is studied by the generation of high order (HHG) harmonics by intense mid-infrared laser pulses. Using an experimental pump-probe method, it is shown that the lattice oscillation introduced by the pump pulse modulates the electron dynamics, and thus the high harmonics, driven by a time-delayed probe pulse.

Nonlinear optical susceptibility of potassium titanyl phosphate

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KTiOPO₄ (KTP) is a very important nonlinear optical material, widely used for second harmonic generation (SHG) of laser light. Despite its widespread use and importance as a nonlinear optical material, there are only very few experimental measurements on its SHG efficiency available. In particular its photon energy dependence has not been systematically studied. Previous theoretical works [1-3] focus mainly on the linear optical properties of KTP.

Our present work aims at closing this gap.

We present a theoretical study of the second-order nonlinear optical susceptibility tensor $\chi^{(2)}$ of KTP from time-dependent density-functional theory. In order to account for excitonic effects, we include the static long-range contribution to the exchange-correlation kernel [4].

Finally, we compare our results with the experimental data.

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Accelerating *GW* Calculations within the LAPW Framework

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The *GW* approach of many-body perturbation theory is an indispensable method for calculating the electronic band structure of solids. Its implementation in computer programs using the linearized augmented plane-wave + local orbital (LAPW+LO) method allows for obtaining numerically precise results [1]. Unfortunately, high precision comes at the price of a large number of LAPWs and LOs. In this work [2], we accelerate *GW* calculations by optimizing the use of LAPWs and LOs in the computer package `exciting` [3]. On the one hand, we introduce a systematic way of obtaining a minimal set of LOs. On the other hand, we perform a basis transformation from the plane-wave part of the LAPWs to different types of basis functions, exploring the efficiency of numeric atom-centered orbitals, Gaussian type orbitals, and Kohn-Sham orbitals. Presenting band gaps of two exemplary materials, zincblende ZnO and hexagonal monolayer BN, we illustrate that our optimization schemes reduce the computational cost down to values as low as 15% without compromising the precision.

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Neural network force fields for simple metals and semiconductors

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We present a practical procedure to obtain reliable and unbiased neural-network-based force fields for solids. Training and test sets are efficiently generated from global structural prediction runs, at the same time assuring structural variety and importance sampling of the relevant regions of phase space. The neural networks are trained to yield not only good formation energies, but also accurate forces and stresses, which are the quantities of interest for molecular dynamics simulations. Finally, we construct, as an example, several force fields for both semiconducting and metallic elements, and prove their accuracy for a variety of structural and dynamical properties. These are then used to study the melting of bulk copper and gold.

Surface spectroscopy of Si(001) surface functionalized with nucleobasis

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Understanding the mechanism of interaction between amino acids and peptides with surfaces opens new perspectives. Adsorption of DNA molecules on semiconducting surfaces is regularly evoked for the design of bio-sensors or the production of bio-materials. The possibility to functionalize surfaces with bio-molecules, to create organized structures up to nanometers' distances depends on our capability to understand precisely the mechanisms which govern the deposition of molecular films onto different kinds of surfaces. For these reasons, this kind of systems have been intensively studied during last decades [1-5].

We present in this poster the results that I have obtained for the Si(001) surface functionalized with two different molecules, the Thymine and the Uracil. The electronic structure has been obtained with a DFT approach, using Abinit [6]. Using DP [7], which allows the calculation of the dielectric response of materials in the TDDFT framework, we computed several surface-related linear spectroscopy quantities (Reflectance Anisotropy Spectrum, adsorbance anisotropy...), that are compared with previous studies [5]. Finally, the code 2Light, which has been recently extended to the case of surfaces [8], has been used to study the Second Harmonic Generation of the Si(001) functionalized with nucleobases.

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Improving Satellite Structures: Dynamical Vertex Correction from Time-Dependent Density-Functional Theory

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Electronic excitation spectra observed in experiments on solid state materials often exhibit strong many-body effects that can be described via many-body theories based on the Greens function formalism. The most popular method employed in practical calculations consists of the GW approximation to the self-energy, which neglects the so-called vertex correction in Hedin's equations [1]. In this approximation, only the change of the coulomb potential due to the density response to the addition or removal of an electron is considered through the microscopic dielectric function ϵ^{-1} . Changes to the exchange-correlation self-energy, instead, are neglected. Although successful for some observables such as band gaps, this method often fails to recover the correct plasmon satellite peaks observed in photoemission experiments. In order to calculate ϵ^{-1} , the density-density response function $\chi(r, r', \omega)$ is needed. A previous study in our group has shown that by including an ω -dependent exchange-correlation kernel in a Time-Dependent Density-Functional Theory calculation of $\chi(r, r', \omega)$, the double plasmon in the dynamic structure factor of sodium is recovered and an overall improvement of calculated spectra is observed as compared to experiment [2]. The way how the exchange-correlation kernel was incorporated in χ relies on the connector approach [3,4] and tabulated calculations of the homogeneous electron gas [2], which include correlations and explicit coupling of excitations. In our current project we set out to further explore the use of this ω -dependent exchange-correlation kernel and the connector to add vertex corrections beyond GW. We present a preliminary study of an analytical model system based on a pure G_0W_0 calculation of sodium.

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Optical properties of eumelanin-functionalized silicon surfaces: Tetramers of DHI-like molecules on Si(001)

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Eumelanin is a photoprotective pigment, widely present in living organisms: it is interesting both for its biological role and in view of possible applications, *e.g.* as a photoactive layer in hybrid solar cells. Porous silicon (PSi) - eumelanin interfaces are interesting systems for photovoltaic applications, due to (a) the large surface-to-volume ratio of the porous substrate,

(b) the peculiar broadband UV-vis absorption spectrum of the pigment, and its biocompatibility and biodegradability. Indeed the ability of eumelanin functionalization to extend the absorption range of PSi towards longer wavelengths has been demonstrated [1,2].

The basic building blocks of eumelanin are 5,6-dihydroxyindole (DHI) - like molecules.

Although the detailed 3D structure of the pigment is not known, a wealth of experimental measurements suggest the presence of locally ordered π -stacked arrangements of relatively small oligomers (like tetramers or pentamers) of DHI-like molecules, and the role of stacking and oligomerization in the emergence of the broadband eumelanin spectrum is actively studied [*e.g.* 3,4]. Computational investigations have been reported on the energetics, adhesion properties, electronic properties, interface stability of simplified models of the PSi-eumelanin interface, consisting of tetramers of DHI-like molecules interacting with the Silicon(001) surface [5,6]. Clearly, a theoretical understanding of the effects of eumelanin on the optical properties of the substrate in these hybrid systems is of paramount importance. First principles calculations on organically functionalized surfaces are able to yield valuable information in this respect (*e.g.* [7]). In this work we investigate, by plane wave density functional theory, the absorption spectra and Reflection Anisotropy Spectra (RAS) of the DHI-like tetramer - functionalized Si(001) surface, focusing on the effect of molecule adsorption, the sensitivity to the type of adsorbed molecule and to its adsorption configuration.

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Energy-level alignment at hybrid organic/inorganic interfaces from first principles: Example of poly(*para*-phenylene) at rock-salt ZnO(100)

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Energy level alignment is a key property that determines the functionality and performance of an (opto-)electronic device. Insights from microscopic simulations are indispensable for a deep understanding of the processes that happen at the interfaces between the active materials. A full *ab-initio* description of real interfaces is an extremely challenging task due to the involved system sizes. Therefore, very often theoretical predictions for the level alignment are based on the superposition of the electronic structures of the individual components. In this work, we explore two such models, widely used for semiconductors, by evaluating them in the context of hybrid materials. For a prototypical hybrid interface, built of poly(*para*-phenylene) and the rock-salt ZnO(100) surface, we perform an *ab-initio* study of the entire system. The quasiparticle description within the G_0W_0 approximation allows us to judge the reliability and shortcomings of the model approaches. By a detailed analysis, we quantify the impact of structure, charge redistribution, orbital hybridization, and molecular polarization on the band offsets and the alignment type - effects that are not or only partially captured by the models.

KTP bulk and defect properties from first-principles calculations

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Potassium titanyl phosphate (KTiOPO₄, KTP) is an important nonlinear optical material with a wide range of applications that profit from its large transparency range, large second harmonic generation (SHG) coefficient and excellent thermal stability [1]. However, many applications require further improvement of the bulk KTP crystal quality in terms of chemical homogeneity, defect structure and optical uniformity. Also, the mechanism of the KTP photochromic damage, called grey tracking, needs to be understood [2]. Our work addresses the KTP structural, electronic and optical properties from first principles considering ideal bulk material as well as intrinsic point defects in the form of O and K vacancies. Ground-state density functional theory is combined with many-body perturbation theory for predictive quality excitation spectra calculations. It is found that quasiparticle effects considerably widen the transport gap to about 5.23 eV, while optical excitations are affected by large exciton binding energies of the order of 1.5 eV. Additionally, oxygen vacancy formation reduces the neighboring Ti⁴⁺ ions to Ti³⁺ and provides a possible explanation for the grey tracking.

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Ground-state correlation energy of beryllium dimer by the Bethe-Salpeter equation and the trace formula

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Since the '30s the interatomic potential of the beryllium dimer Be_2 has been both an experimental and a theoretical challenge. Calculating the ground-state correlation energy of Be_2 along its dissociation path is a difficult problem for theory. We present *ab initio* many-body perturbation theory calculations of the Be_2 interatomic potential using the GW approximation and the Bethe-Salpeter equation (BSE). The ground-state correlation energy is calculated by the trace formula with checks against the adiabatic-connection fluctuation-dissipation theorem formula. We show that inclusion of GW corrections already improves the energy even at the level of the random-phase approximation. At the level of the BSE on top of the GW approximation, our calculation is in surprising agreement with the most accurate theories and with experiment. It even reproduces an experimentally observed flattening of the interatomic potential due to a delicate correlations balance from a competition between covalent and van der Waals bonding.

Modeling of blue light pathways in light harvesting complexes

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Biological systems developed complex molecular machineries able to convert solar energy into biochemical fuel and also to store it in an efficient way that could not be replicated so far.

Although this light interaction has been known for about two centuries and has been comprehensively studied from both experimental and theoretical view, the flow of high-energy excitations in biological light-harvesting complexes (LHCs) is still not fully understood.

Especially, the mechanism of the energy flow from carotenoids to chlorophylls exhibits gaps of understanding [1]. We are investigating the blue light pathways of strongly coupled chromophores in light harvesting complexes and to what extent they compete with common internal conversion processes. We are focusing on the antenna complex CP29 [2-3], which is part of the PSII supercomplexes and present in algae, spinach and other plants.[4-5] Here the influence of the single components on the optical behavior is analyzed to obtain a accurate description of the spectrum. The investigation of the spectral and conformational properties of

biological chromophores are computed using density functional theory and other cost-efficient quantum chemical methods like QM/MM. To get an idea of the conformational space and the intermolecular interactions it is necessary to deviate from the crystal structure by applying molecular dynamics on the system.

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Exciton-Phonon Coupling in Monolayer and Bilayer MoTe₂

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MoTe₂ belongs to the family of group VI layered transition metal dichalcogenides (TMD), whose structure is composed of two-dimensional (2D) sheets weakly bound by Van-der-Waals interactions. These materials have been extensively studied for their exceptional properties: electronic, optical and for the appearance of topological or superconducting phases [1–3]. In the hexagonal form, they generally show a clear photo-luminescence (PL) signal in the IR-VIS range when monolayers, while the PL becomes almost absent in the bilayer, multi-layer and bulk. This has been explained by an indirect-to-direct bandgap crossover [4] and by the presence of strongly bound excitons with fast radiative lifetimes [5] occurring in the monolayer. Nevertheless MoTe₂ shows a much stronger PL signal with respect to the other group-VI TMDs in the bilayer (BL) form but the origin of this behaviour has not yet been clarified. Indeed, while some experiments conclude about the presence of a direct gap also in the BL [1,3], theoretical simulations seem to agree on an indirect gap nature like in the other MX₂ [2]. Our aim is then to investigate this issue using Density Functional Theory (DFT), Many Body Perturbation Theory (MBPT) and Density Functional Perturbation Theory (DFPT). On one side we will investigate the role of the strain on the electronic bandstructure and optical properties of MoTe₂ BL looking for a possible indirect to direct bandgap crossover. On the other side, in a similar way to what has been recently done for h-BN by some of us [6], exploiting nondiagonal supercells [7,8] to reduce the computational cost, we will use innovative methods to take into account the coupling between excitons and phonons [8] to calculate the optical spectrum of MoTe₂ BL, in order to see how it is modified by this interaction.

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Theoretical description of non-linear processes in magnetic materials

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Chromia (Cr₂O₃) is a typical Mott Hubbard anti-ferromagnetic insulator in the class of transition metal oxides. Cr₂O₃ is an ideal material to demonstrate ultra-fast control of demagnetization at higher speed. Ultra-fast control on the magnetic state could have the strong impact on magnetic recording technology. Second harmonic generation (SHG) is a process where two photons are absorbed by a material, and a photon of twice the energy of the incoming photons is emitted. This spectroscopy is used to study the optical properties of materials because it reveals additional information, compared with linear optical spectroscopies. Due to dipole selection rules, SHG is forbidden in centrosymmetric materials, and it is possible to obtain a structural and electronic characterization for these systems. However, the absence of time-inversion symmetry in antiferromagnetic materials leads to new contributions in the second harmonic generation, thus revealing the arrangement of spins in the solid. SHG becomes a powerful tool to study of ultra-fast demagnetization processes. There are few satisfactory theoretical descriptions for SHG in magnetic materials, since spin-orbit coupling, electron-electron interactions, and local field effect must be treated on the same footing. The project is to calculate the Second order response function of Cr₂O₃ using Time-Dependent Density Functional Theory, and taking into account the many-body effects through an exchange-correlation kernel derived from the Bethe-Salpeter equation for the linear response. Results will be shown for the linear response and the GW corrected band gap for the Cr₂O₃. Preliminary results will also be also presented for the BSE calculations.

Local mixing in modified Becke-Johnson potential for reliable description of heterostructure interfaces and surfaces

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Modified Becke-Johnson (MBJ) exchange-correlation potential (also often referred to as Tran-Blaha potential) [1] is known as one of the best approximations to the exchange-correlation potential for calculations of band gaps of solids using density-functional theory. It is designed as a sum of two terms with a material dependent mixing factor c which governs the amount of the two constituents and is calculated self-consistently from the electronic density and its gradient in the whole unit cell.

In this work we follow the approach of local hybrid functionals [2,3] and evaluate the mixing locally as $c(\mathbf{r})$. We implemented our method in the *Vienna ab-initio simulation package* code [4]. We first confirmed that the MBJ band gap values of bulk materials are recovered when using an appropriate smearing of $c(\mathbf{r})$ and then calculated the electronic properties of chosen semiconductor heterostructures. We obtained correct band gaps in the bulk regions also for the heterostructures, in contrast to the GGA-PBE [5] functional or the original Tran-Blaha potential. The calculated valence and conduction band offsets show values varying between “as wrong as GW” and “better than GW”. Finally, we applied a second modification to the MBJ potential which enables us to use it for surfaces and other systems with vacuum, in contrast to the original version. As for the heterostructures, we obtained here the correct band gap in the bulk region. The quality of the calculation of surface properties such as the work function using our approach is yet to be evaluated.

We thus expand the field of usage of the MBJ potential from periodic bulk materials only to heterostructures and surfaces, which should enable other researchers to model the electronic properties of these systems with the accuracy reaching the one of hybrid functionals or even GW, while paying the much lower costs of metaGGA calculations.

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Electronic properties of two-dimensional hexagonal boron nitride (2D-hBN) superstructures

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In the last years 2D materials have attracted much interest in fundamental research and practical applications because of their unique physical properties. From the multitude of existing 2D materials even van der Waals based heterostructures can be created just by vertically stacking, which may provide entirely new physical effects. The here investigated hBN thereby plays an important role because of its suitability to serve as a passivation layer. One of the possibilities to synthesize 2D-hBN is chemical vapor deposition (CVD) of borazine on (111) surfaces of transition metal single crystals. The choice of the substrate thereby play an important role as it directly changes the structural and electronic properties of the created overlayer. For this reason we investigated the chemical as well as the electronic properties of 2D-hBN on three different substrates. In all cases hBN forms superstructures with high structural quality; however, different morphologies were obtained: a flat monolayer is formed on Ni(111), a slightly corrugated layer on Pt(111), and a highly corrugated layer is formed on Rh(111), the so-called nanomesh. The chemical and local atomic structure of each hBN layer was studied by means of x-ray photoelectron spectroscopy (XPS) and x-ray photoelectron diffraction (XPD) in forward scattering geometry, respectively. The band structure was measured with angle resolved ultraviolet photoelectron spectroscopy (ARUPS) and compared to density functional theory (DFT) calculations of a freestanding hBN monolayer. Lattice properties were investigated using low energy electron diffraction (LEED).

Influence of quasiparticle and excitonic effects on the optical signatures of polarons and bipolarons in LiNbO_3 from *ab initio* calculations

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Lithium niobate (LiNbO_3), a perovskite-structure ferroelectric, is widely employed in nonlinear optical applications. A direct comparison between experiment and theory is difficult, however, as this material exhibits a large concentration of intrinsic defects, which strongly influence the optical properties. To reproduce the so-called polaron and bipolaron peaks found in the experimental measurements of the absorption spectrum, we test different defect types. The results shed light on the possible origin of the observed peaks due to the different optical characteristics of the investigated defects.

Polarization anisotropies at x-ray absorption edges

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H. Bernhardt,^{1,2} R. Loetzsch,^{1,2} H.-C. Wille,⁴ R. Röhlberger,⁴ and G. G. Paulus^{1,2}

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Investigation of optical anisotropies, namely dichroism and birefringence, at an X-ray absorption edge showed that birefringence has a remarkable influence on polarization resolved spectroscopy measurements. High precision X-ray polarizers with a polarization purity of 10^{-8} enabled intensity dynamics of six orders of magnitude. We investigated two different crystal systems, orthorhombic La_2CuO_4 and monoclinic CuO , and revealed a signature of the non-diagonal tensor elements of the complex linear absorption coefficient on the $\sigma - \pi$ scattered photons. Ab initio simulations by the FDMNES [1] code allowed detailed comparison of dichroism and birefringence with the experiment.

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CuI as Potential *p*-type Transparent Conductor: Electronic and Optical Properties from First Principles

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The lack of viable *p*-type transparent conductors represents a critical bottleneck for future transparent electronics. CuI, with its direct band gap of 3.1 eV and its demonstrated *p*-type conductivity, is a promising candidate for such a material. Recently, it has raised significant renewed interest due to the production of transparent conducting bipolar CuI/ZnO heterostructure diodes, its applications as hole collection layer in organic electronics, or as promising candidate for a flexible, transparent thermoelectric material. However, a detailed theoretical understanding of the optical properties of CuI is still missing.

We use density-functional theory and many-body perturbation theory to study the structural, elastic, electronic, and optical properties of CuI in the zincblende structure (also known as the room-temperature γ phase), as well as for the hexagonal β phase. We have calculated key quantities of its electronic structure, in particular the band gap, effective electron and hole masses, and spin-orbit-coupling induced band splittings and compare them to available experimental values. Furthermore, we explore the optical absorption properties in the vicinity of the band gap heading towards the inclusion of excitonic effects.

Spatially Resolved Fourier Transform of Induced Density from δ -Kick Time-Evolution Calculation

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Within the framework of Time-Dependent Density-Functional Theory, the real-time (RT-TDDFT) propagation scheme of Yabana and Bertsch [1] gives direct access to the density dynamics and related quantities (dipole, absorption spectra...). However, in comparison with transition-based linear-response (LR-TDDFT) calculations the results of RT-TDDFT are relatively difficult to interpret due to the lack of direct information on the origin of spectral features. We analyze the time-dependent density from δ -kick time-evolution calculations using spatially resolved Fourier transformation [2,3]. In this way, we obtain spatial information about the origin of individual peaks in the spectra which are comparable to the transition densities obtained in LR-TDDFT calculations. Individual modes are recovered from the Fourier coefficients and can be identified using color maps and animations. The differences between collective plasmonic excitations and the excitations involving d-electrons, as well as the interplay between them are captured in this analysis. In ligand-protected Ag₂₉(BDT)₁₂(TPP)₄ cluster, the analysis reveals that the low-energy excitations are confined to the Ag core of the compound, unlike the strong high-energy excitations, which are found to have principal contributions from the benzene rings of the surrounding ligands. In more complex monolayer protected Au₁₄₄(+ligands) clusters this analysis is employed to capture the origin of differences in the spectral features when two different ligands are chosen.

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Direct Insight into the Structure-Property Relation of Grain Boundaries From First-principles Crystal Structure Prediction

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A major issue that prevents a full understanding of heterogeneous materials is the lack of systematic first-principles methods to predict consistently both energetics and electronic properties of reconstructed interfaces. In this work we develop an efficient and accurate computational scheme aimed at solving this problem. Our approach is a variant of the minima-hopping method for global crystal structure prediction, conceived for quasi-two-dimensional systems. Specifically, we implement a constrain library crafted for two-dimensional atomic relaxation and we enable variations of the atomic density in proximity to the interface. Density-functional and density functional tight-binding calculations supply necessary energy and forces to the minima-hopping algorithm. We demonstrate the power of this method by applying it to extract structure-property relations for a varied family of symmetric and asymmetric tilt boundaries in polycrystalline silicon. We find a rich polymorphism in the reconstructions of the grain boundaries, with recurring bonding patterns that we classify in increasing energetic order. In several cases, we succeed in identifying atomic arrangements that are significantly more stable than previously predicted structures, while in other cases we show that the algorithm can recover, without experimental input, geometries that had been build by hand to match experimental data. Finally, a clear relation between bonding patterns and electrically active interface states is unveiled and discussed.

Towards a theoretical description of ultrafast transport phenomena

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Ultrafast spin-dependent transport and angular momentum decrease are highly interesting topics of current research [1-3]. We discuss laser-induced electron-hole excitations and reoccupation as reasons for those effects. On that account we show the principles of demagnetization by means of electronic redistribution within a minimalistic tight-binding based 4-state model. In addition, we analyze the time evolution of electronic occupation numbers calculated with time-dependent density functional theory [4]. These are used to compute the internal time-dependent spin current caused by the laser excitation.

Furthermore, we present a possible application of ultrafast processes in form of so-called optically controlled magnetoresistance where a significant resistance change can be achieved due to laser-induced magnetization switching in a heterostructure.

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Reliable *Ab Initio* Methodology to Compute Electronic Properties of Organic-Inorganic Metal Halide Perovskites

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In the last decade, organic-inorganic metal halide perovskites have attracted enormous interest as promising materials for photovoltaic applications. To study these complex compounds, an accurate, computationally affordable, and transferable methodology from first principles is required. Here, we investigate the electronic structure of these materials in the frameworks of density-functional-theory and many-body perturbation theory (MBPT). We focus on hybrid exchange-correlation functionals as a potential alternatives to the more computational expensive *GW* approach of MBPT. In these functionals, the Hartree-Fock (HF) exchange is mixed with a local or semi-local exchange correlation functional. The ratio of HF is given by the mixing parameter α , and in HSE06, also by the screening parameter ω . We observe that the standard parameters of PBE0 and HSE06 are not suitable for metal halide perovskites, since they severely underestimate their energy gaps. Therefore, we explore several methods to determine optimal parameters, which reproduce the effective screening of these materials. Furthermore, the presence of heavy elements like lead, requires a careful treatment of the spin-orbit coupling, since it crucially impacts the electronic band gaps of these systems. We compare the exact treatment, obtained by solving the Dirac equation in spinor form, with a perturbative approach, and we assess their performance in terms of precision and computational cost.

How Metallic are Tiny Pieces of Noble Metals? Metallicity and Screening in Gold and Silver Clusters

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Metallicity of nanoparticles can be defined in different ways. One commonly used possibility is to look at the degree to which external fields will be screened inside the object. This screening would be complete in a classical perfect metal where surface charges arrange on the classical — i.e., abrupt — surface such that no internal fields exist. However, it is obvious that this situation is modified for very small clusters: the surface charges are “smeared out” at the surface, and the screening might be less complete. In the present work we ask the question as to how close small noble-metal clusters are to the classical situation. We show that, indeed, the screening is almost complete already for as little as two atomic layers of the metals, silver and gold alike. At the same time, we show that quantum effects play a role, meaning that the clusters cannot be described solely using the concept of classical screening in a classical metal.

We demonstrate these points using realistic atomistic pseudopotential density-functional theory (DFT) calculations, along with jellium-based DFT calculations which can be interpreted more easily than their pseudopotential counterparts. The dynamic response of the system to a time-dependent external perturbation is discussed using induced densities from time-dependent DFT.

Modelling the hydrogen molecule with unrestricted generalized Kohn-Sham theory

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Unrestricted Hartree-Fock (UHF) theory is known to correctly describe the energy and electron density of the dissociated hydrogen molecule (H_2); however, at the bonding length these quantities are inaccurate due to a lack of dynamic correlation. Calculations beyond HF within many-body perturbation theory are computationally expensive. On the other hand, Kohn-Sham (KS) theory is computationally cheap but is known to require a local exchange-correlation potential which possesses pathological features when atoms disassociate. We employ the exchange operator of UHF and HF within generalized KS (GKS) theory for a one-dimensional model of H_2 with varying atomic separation: the exact correlation potential which corresponds to UHF's exchange operator is shown to be free of these pathological features and hence a local density approximation to its correlation energy performs well for the electron energy and density at any atomic separation.

On the (topological) low-energy phases of bismuthene

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Topological properties have been recently measured in bismuth monolayers (bismuthene) grown on a SiC substrate [1]. It is known that the hexagonal phase observed is not the ground state of the free standing system, and others might exist. We develop [2] an ab-initio structure search algorithm, to systematically explore the configuration space of materials confined in quasi-2D. Using this approach we discover several novel metastable phases of bismuthene, in addition to the two known structures. In this talk, we will show that these phases exhibit very different electronic properties including metallic, semiconducting, and non-trivial topological insulating phases, and could be stabilized by a suitable choice of substrate and/or strain. In particular, we predict a Bi phase which is topologically non-trivial already in the freestanding 2D case, presenting symmetry-protected topological Dirac points.

[1] Reis et al, Science 357, 287 (2017)

[2] S. Singh, Z. Zanolli, M. Amsler, B. Belhadji, J. O. Sofo, M. J. Verstraete, A. H. Romero, Low energy phases of bilayer Bi predicted by structure search in two dimensions
<https://arxiv.org/abs/1901.05060>.

Monday 16 September		
Time	Duration	Speaker
13:30	02:00	ETSF SC
15:30	00:30	Reg. & coffee
16:00	00:10	Opening
16:10	00:45	Reining
16:55	00:45	Scheffler

19:00	02:00	Welcome evening
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Tuesday 17 September		
Time	Duration	Speaker
09:00	00:40	Kioupakis
09:40	00:20	Sponza
10:00	00:20	Bechstedt
10:20	00:30	Coffee break
10:50	00:40	Urbaszek
11:30	00:20	Melo
11:50	00:20	Maruhn
12:10	02:00	Lunch
14:10	00:40	Romaniello
14:50	00:20	Laricchia
15:10	00:20	Panholzer
15:30	00:30	Coffee break
16:00	00:20	Patterson
16:20	00:20	Helbig
16:40	03:20	Poster session

Wednesday 18 September		
Time	Duration	Speaker
09:00	00:40	Grüning
09:40	00:20	Véniard
10:00	00:20	Deilmann
10:20	00:30	Coffee break
10:50	00:20	Aouina
11:10	00:20	Godby
11:30	00:40	ETSF GM
12:10	02:00	Lunch
14:10	00:40	Vandewal
14:50	00:20	Ortmann
15:10	00:20	Quarti
15:30	00:30	Coffee break
16:00	00:20	Poloni
16:20	00:20	Gruenewald
16:40	00:20	Suckert
17:00	00:15	Break
17:15	00:30	Paulus
17:45	00:30	Eggeling

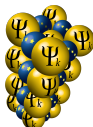
Thursday 19 September		
Time	Duration	Speaker
09:00	00:40	Perfetti
09:40	00:20	Krasovskii
10:00	00:20	Otto
10:20	00:30	Coffee break
10:50	00:40	Sangalli
11:30	00:20	Alvertis
11:50	00:20	Chen
12:10	02:00	Lunch
14:10	00:40	Gräfe
14:50	00:20	Koskelo
15:10	00:20	Giorgetti
15:30	00:30	Coffee break
16:00	00:20	Friedrich
16:20	00:20	Taudul

17:30	01:30	Guided tour
19:00	06:00	Workshop dinner

Friday 20 September		
Time	Duration	Speaker
09:00	00:40	Schnohr
09:40	00:20	Aldahhak
10:00	00:20	Rokaj
10:20	00:30	Coffee break
10:50	00:40	Cocchi
11:30	00:20	Reshetnyak
11:50	00:20	Vorwerk
12:10	00:10	Closing remarks



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DOWN TO ATOMIC SCALES

