Report Psi-K / CECAM workshop
“Ultrafast Physics from molecules to nanostructures”

Dates: 7-10 October 2019
Location: San Sebastian (Spain)

We have gathered world-leading experimental, theoretical and computational experts working in the field of electronic and nuclear dynamics in atoms, molecules and solids. These four days have provided a unique cross-fertilization opportunity to advance the current ab-initio state-of-the-art approaches. Several key and crucial questions have been vividly and intensely debated: how to extend the accuracy of ab-initio methods out-of-equilibrium? How to efficiently benefit from the advances in computation facilities to simulate the nonequilibrium dynamics of large molecules, nanostructures and solids? How to translate laser-pulse features (pulse center frequency, bandwidth, duration, fluence, polarization) into boundary conditions and suitable approximations for the computational tools? Can we devise a series of tools and procedures to provide to the community? We have also confronted different theoretical formulations of experimental outcomes, discuss their range of applicability as well as their physical and numerical limitations. For the various approaches we have explored how to include the missing physics and whether this inclusion is numerically feasible.

Program:

1. Ultrafast Quantum Photonics - Monday

14:00 - 14:45 - Alfred Leitenstorfer (Keynote)
TBA
14:45 - 15:20 - Martin Schultze (Contributed)
Light-wave driven charge- and spin dynamics probed by attosecond X-rays
15:20 - 15:50 - Break
15:50 - 16:25 - Andrea Cavalleri (invited)
TBA

2. Low-dimensional materials - Tuesday

9:00 - 9:45 - Ralph Ernstorfer (keynote)

Ultrafast multidimensional photoemission spectroscopy and diffraction of nanoscale materials

9:45 - 10:20 - Marco Bernardi (invited)

TBA

10:20 - 10:50 - Break

10:50 - 11:25 - Hannes Hubener (invited)

TBA

11:25 - 12:00 - Martin Eckstein (invited)

Cold photo-induced phases in quantum materials

12:00 - 12:25 - Pedro Melo (contributed)

Spin States Protected from Intrinsic Electron−Phonon Coupling in MoSe2

12:25 - 14:00 - TAPAS lunch (organized)

3. Attosecond dynamics in molecules and nanostructures (I) - Tuesday

14:00 - 14:45 - Marc Vrakking (keynote)

TBA

14:45 - 15:20 - Thomas Pfeifer (invited)

Quantum dynamics and control around the 1-fs time scale: Driving excited states in atoms and molecules with intense light from the NIR to the XUV

15:20 - 15:50 - Break

15:50 - 16:25 - Walter Pfeiffer (invited)

Attosecond dynamics in solids after photoexcitation as a benchmark for our understanding of complex quantum systems

16:25 - 17:00 - Enrico Perfetto (invited)

First-principles nonequilibrium Green's function approach to real-time simulations of correlated electrons in molecular systems

17:00 - 17:25 - Tuomas Rossi (Contributed)

Ultrafast Dynamics of Plasmons and Strong Plasmon-Molecule Coupling at the Nanoscale: Insights from First-Principles Modeling

4. Soft X-ray spectroscopy - Wednesday

9:00 - 9:45 - Jens Biegert (Keynote)

TBA

9:45 - 10:20- Emma Springate (invited)

TBA

10:20 - 10:50 - Break

10:50 - 11:25 - Luca Perfetti (invited)

Hot carriers and screening effects in a two dimensional electron gas on InSe

2. Low-dimensional materials - Wednesday

11:25 - 11:50 - Valerie Smejkal (Contributed)

Simulation of the Ultrafast Exciton Buildup in Monolayer MoS_2

11:50 - 12:15 - Stefano Calati (Contributed)

Dynamic Screening of Quasiparticles in WS_2 Monolayers

12:15 - 14:00 - Lunch (free)

5. Theoretical and computational methods for systems out of equilibrium - Wednesday

14:00 - 14:45 - Irene Burghardt (Keynote)

Ultrafast Quantum Dynamics of Functional Organic Polymer Materials: Coherence, Confinement, and Disorder

14:45 - 15:20 - Davide Sangalli (invited)

ab-initio description of pump and probe experiments: from carriers to exciton dynamics

15:20 - 15:50 - Break

15:50 - 16:25 - Simone Latini (invited)

TBA

16:25 - 17:00 - Sangeeta Sharma (invited)

TBA

17:00 - 17:25 - Sivan Refaely-Abramson (Contributed)

New Insights into complex exciton phenomena in materials from many-body perturbation theory

6. Attosecond dynamics in molecules and nanostructures (II) - Thursday

9:00 - 9:45 - Ivano Tavernelli (Keynote)

TBA

9:45 - 10:20 - Fernando Martin (invited)

Attosecond pump-probe spectroscopy of molecular electron dynamics: a theoretical point of view

10:20 - 10:50 - Break

10:50 - 11:25 - Aaron Kelly (invited)

Trajectory-based Approaches to Quantum Dynamics: Wavefunctions, Density Matrices, and Master Equations

11:25 - 12:00 - Christian Schaefer (invited)

Ab initio cavity QED - dipping the toe into cavity chemistry

12:00 - 12:25 - Peter Saalfrank (Contributed)

Correlated wavefunction approaches to laser-driven electron dynamics in molecules and their control
12:25 - 14:00 - TAPAS lunch (organized)

7. Natural and artificial light harvesting - Thursday

14:00 - 14:45 - Alexandra Olaya-Castro
TBA
14:45 - 15:20 - Erling Thyrhaug (invited)
TBA
15:20 - 15:50 - Break
15:50 - 16:25 - Akshay Rao (invited)
16:25 - 17:00 - Joel Yuen-Zhou (invited)
TBA
17:00 - 17:25 - Vasil Rokaj (Contributed)
QED-Bloch Theory with Homogeneous Magnetic Fields: Modifications of the Landau Levels and the Hofstadter Butterfly

List of titles and abstracts:

1. Ultrafast Quantum Photonics

Alfred Leitenstorfer (Keynote)

Martin Schultze (invited)
Light-wave driven charge- and spin dynamics probed by attosecond X-rays

After influential experiments in atomic and molecular systems, since a few years attosecond soft-X-ray pulses permit time resolved spectroscopy of electron dynamics in solid-state systems providing us with a time-domain understanding of light-matter interactions also in the condensed phase. As example, I will discuss experiments scrutinizing the electron excitation dynamics in metals and semiconductors and present results of the extension of the technique to follow ultrafast spin-dynamics in ferromagnetic structures.

Andrea Cavalleri (invited)

2. Low-dimensional materials

Ralph Ernstorfer (keynote)

Ultrafast multidimensional photoemission spectroscopy and diffraction of nanoscale materials

The dynamics of quasi-particles in non-equilibrium states of matter reveal the underlying microscopic coupling between electronic, spin and vibrational degrees of freedom. We aim for a quantum-state-resolved picture of coupling on the level of quasi-particle self-energies, which goes beyond established ensemble-average descriptions, and which requires ultrafast momentum- resolving techniques. The dynamics of electrons and excitons is measured with four-dimensional time- and angle-resolved photoelectron spectroscopy (trARPES), featuring a high-repetition rate XUV laser source [1] and momentum microscope detector, see Fig. 1. I will exemplify this experimental approach by discussing electron and exciton dynamics in the semiconducting transition metal dichalcogenide WSe2 [2] and discuss its extension to nanoscale heterostructures. Upon strong excitation inducing phase transitions, trARPES reveals the full transient electronic structure driving the structural transition along the reaction coordinate [3]. The complementary view of ultrafast phonon dynamics is obtained through inelastic femtosecond electron diffraction [4].

References:

[1] M. Puppin et al., Rev. Sci. Inst. 90, 23104 (2019).
[2] R. Bertoni et al., Phys Rev. Lett. 117, 277201 (2016).
[3] C.W. Nicholson et al., Science 362, 821 (2018); Phys. Rev. B 99, 155107 (2019
[4] L. Waldecker et al., Phys. Rev. Lett. 119, 036803 (2017).

Marco Bernardi (invited)

Hannes Hubener (invited)

Martin Eckstein (invited)

Cold photo-induced phases in quantum materials

Ultrafast laser induced transitions can potentially induce novel phases in correlated electron materials. However, a challenge to overcome is that a rapid, quench-like photo-excitation usually deposits enough entropy in the system to melt any subtle low-temperature phase. Here we discuss a protocol which allows to generate "cold" photo-doped states, with a low entropy density, on fast timescales [1]. In simulations on the Fermi-Hubbard model, this has been shown to drive a system into the elusive eta-pairing superconducting phase [2].

[1] Philipp Werner, Martin Eckstein, Markus Müller, Gil Refael, Cooling by photo-doping –– Light-induced symmetry breaking in the Hubbard model, arXiv:1904.00822.
[2] Jiajun Li, Denis Golez, Philipp Werner, Martin Eckstein, Long-range η-pairing in photodoped Mott insulators, arXiv:1908.08693

Pedro Melo (contributed)

Spin States Protected from Intrinsic Electron−Phonon Coupling in MoSe2

Measurements in monolayer MoSe2 of the Kerr rotation have show spin lifetimes of over 100 ns at room temperature. These are also accompanied by a non monotone temperature dependence of the Kerr amplitude, which increases with temperature up to 50 K, having then an abrupt sign change. With ab initio simulations we can explain the latter behaviour as an effect of the intrinsic electron-phonon coupling and possibility of electrons to transit into secondary valleys. The electron-phonon scattering mechanism begins this scattering process within the first picoseconds after excitation. The sign of the resulting magnetisation, and so the Kerr amplitude as well, changes signal as a function of temperature, as electrons and holes have different changes in intervalley scattering rates. Our ab initio calculations do not, however, provide a reason for the long spin lifetimes. This leads us to the conclusion that the some of the initial spin polarisation must be stored into spin states which are protected from the intrinsic electron-phonon interaction. These states are most likely resident charge carriers, which are not part of the itinerant valence or conduction band states.

3. Attosecond dynamics in molecules and nanostructures (I)

Marc Vrakking (keynote)

Thomas Pfeifer (invited)

Quantum dynamics and control around the 1-fs time scale: Driving excited states in atoms and molecules with intense light from the NIR to the XUV

Electronic states in atoms and molecules can be dressed by intense laser fields, giving rise to well-known phenomena such as Rabi oscillations and Stark shifts when the fields last long enough. What happens for intense, pulsed driving fields, shorter than the characteristic time scales of interest (lifetimes and inverse level spacings) remained largely unexplored.

Here, we shed intense broadband and ultrashort optical (NIR) and extreme ultraviolet (XUV) light on a range of dynamical processes, including Fano resonances (based on correlated-particle quantum interference), inner-valence excitations (relevant for site-selective spectroscopy), and ionic resonances after multiple ionization by free-electron laser pulses (playing a role in x-ray imaging and concomitant radiation damage). We experimentally observe, respectively, effects of controlled impulsive phase shifts on specific excited states, uncover spectroscopic information on otherwise dipole-forbidden transitions, and 2-femtosecond coherence effects in pump-probe transient-absorption experiments with stochastic SASE FEL pulses.

These results provide building blocks for the road towards multidimensional multi-color spectroscopy near core resonances to observe electron motion between specific sites in molecules with sub-femtosecond resolution. The bound-state control mechanisms experimentally demonstrated here can be understood as state-selective handles for direct quantum control of wavepacket phases in a multitude of systems from isolated atoms to condensed-phase molecules.

Walter Pfeiffer (invited)

Attosecond dynamics in solids after photoexcitation as a benchmark for our understanding of complex quantum systems

In recent years, time-resolved spectroscopy of electron dynamics in solids advanced to the attosecond regime, i.e. on the time scale on which electron motion occurs on an atomic scale. In such experiments an extreme ultraviolet (EUV) pulse with durations of typically a few 100 as is used to excite the solid and the response is probed by correlating this excitation with a field in the near infrared (NIR). One example of such a technique is attosecond time-resolved streaking spectroscopy [1]. This technique allows investigating relative temporal delays in the photoemission from different initial states. Discrepancies between experimental observations and existing theoretical models challenge our understanding of the photoemission process. Using this technique we were recently able to demonstrate that the present theoretical model of solid state photoemission misses an essential effect that significantly affects such photoemission delays [2]. Intra-atomic delays determined by the involved angular momentum of the photoelectron affect the photoemission times and are not accounted for in present theoretical models of solid state photoemission. In our present approach to describe the observations we dissect the photoemission process artificially in an intra-atomic and a propagation part that are modeled based on theoretical concepts from atomic physics and solid state physics, respectively. To overcome this artificial dissection new theoretical models of the photoemission process are needed and, hence, attosecond time-resolved spectroscopy provides new benchmarks for a further development of a complex quantum system, i.e. the dynamics of the many-body problem of a photoelectron interacting with the remaining photohole and the other electrons.

1. A. L. Cavalieri, N. Müller, T. Uphues, V. S. Yakovlev, A. Baltuska, B. Horvath, B. Schmidt, L. Blumel, R. Holzwarth, S. Hendel, M. Drescher, U. Kleineberg, P. M. Echenique, R. Kienberger, F. Krausz, U. Heinzmann, Attosecond spectroscopy in condensed matter. Nature. 449, 1029–1032 (2007).

2. F. Siek, S. Neb, P. Bartz, M. Hensen, C. Strüber, S. Fiechter, M. Torrent-Sucarrat, V. M. Silkin, E. E. Krasovskii, N. M. Kabachnik, S. Fritzsche, R. D. Muiño, P. M. Echenique, A. K. Kazansky, N. Müller, W. Pfeiffer, U. Heinzmann, Angular momentum–induced delays in solid-state photoemission enhanced by intra-atomic interactions. Science. 357, 1274–1277 (2017).

Enrico Perfetto (invited)

First-principles nonequilibrium Green's function approach to real-time simulations of correlated electrons in molecular systems

We show how to describe the correlated electron dynamics of molecules and molecular complexes driven by ultrafast laser pulses using the first-principles nonequilibrium Green's function (NEGF) method [1-5]. The method is currently implemented in the CHEERS code [6] which allows for addressing a broad variety of time-resolved phenomena such as transient photoabsorption and photoemission, time-resolved Auger decays as well as ultrafast charge migration. CHEERS is compatible with all main single-particle basis functions (plane-waves, Gaussian type orbitals, Slater type orbitals, real-space grid etc.) and it accounts for both static and dynamical correlation effects.

In this talk we discuss how the proposed method is used to address the charge migration process in biological molecules [7], a topic of high current interest to unravel the fundamental mechanisms at the basis of photo-protection or photo-damage. The role played by correlations and memory effects is crucial to achieve an excellent agreement with available experimental data [7-9].

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[2] E. Perfetto, A.M. Uimonen, R. van Leeuwen and G. Stefanucci, Phys. Rev. A 92, 033419 (2015).

[3] F. Covito, E. Perfetto, A. Rubio and G. Stefanucci, Phys. Rev. A 97, 061401(R) (2018).

[4] D. Karlsson, R. van Leeuwen, E. Perfetto and G. Stefanucci, Phys. Rev. B 98, 115148 (2018).

[5] E. V. Boström, A. Mikkelsen, C. Verdozzi, E. Perfetto and G. Stefanucci, Nano Lett. 18, 785 (2018).

[6] E. Perfetto and G. Stefanucci, Journal of Physics: Condensed Matter 30, 465901 (2018).

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Tuomas Rossi (Contributed)

Ultrafast Dynamics of Plasmons and Strong Plasmon-Molecule Coupling at the Nanoscale: Insights from First-Principles Modeling

Localized surface plasmons render metal nanoparticles efficient light absorbers at their resonance frequencies. After light absorption by the collective plasmon mode, the system can display different femtosecond-scale processes: The plasmon oscillation can decay non-radiatively and lose its energy to incoherent high-energy electrons and holes, or a

coherent energy exchange can take place between plasmon and other strongly-coupled electronic excitations, manifested as Rabi oscillations. Such ultrafast processes, combined with the large photoabsorption cross section, make plasmonic nanoparticles an attractive platform for photocatalysis and emerging quantum optics applications.
In this presentation, we employ time-dependent density-functional theory (TDDFT) for providing first-principles insights on these ultrafast processes at the nanoscale. In particular, we analyze the electron-hole transitions involved in the photoabsorption and in the subsequent dynamics of the electronic system, which enables us to scrutinize the plasmonic character [1], follow the plasmon decay into hot electrons and holes [2], quantify the direct hot-carrier transfer to the environment [3], and dissect the symmetric and antisymmetric hybrid modes caused by strong coupling between plasmon and molecular excitation [4]. Our work paves the way for addressing spatiotemporal dynamics of plasmon-enhanced processes down to the atomic-scale details, which on a broader perspective enables parameter-free exploration of desired material properties.
[1] T. P. Rossi, M. Kuisma, M. J. Puska, R. M. Nieminen, and P. Erhart, J. Chem. Theory Comput. (2017). https://doi.org/10.1021/acs.jctc.7b00589
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4. Soft X-ray spectroscopy

Jens Biegert (Keynote)

Emma Springate (invited)

Luca Perfetti (invited)

Hot carriers and screening effects in a two dimensional electron gas on InSe

The van der Waals chalcogenides display a variety of different specifics that depend on their composition and number of layers. Weak mechanical binding of atoms along the stacking direction facilitates the realization of heterostructures with different functionalities. Some recent achievements have been the fine tuning of the band gap, the control of valley polarization, and the realization of devices with high mobility. In this context, InSe is one of the building blocks with the highest potentials. The bulk crystals of InSe can be thinned downto a fewlayers and encapsulated in hexagonal boron nitride (hBN). By these means, It has been possible to fabricate transistors whose quality is high enough to observe Shubnikov–de Haas oscillations and the quantum Hall effect. These results point out the two aspects making InSe particularly appealing. On one hand, the

mobility of charge carriers rivals the one measured in graphene. On the other hand, the bulk band gap of 1.26 eV is ideally suited for optoelectronic devices. Indeed, several groups have recently reported that InSe and graphene/InSe heterostructures have excellent photoresponsivity in the visible spectral region. In the first part of the talk I will discuss the dynamics of hot carriers in InSe on the femtosecond regime. The electrons excited by photons of 3.12 eV experience a manifold relaxation. First, they thermalize to electronic states degenerate with the M valley. Subsequently, the electronic cooling is dictated by Fröhlich coupling with phonons of small momentum transfer. Ab initio calculations predict cooling rates that are in good agreement with the observed dynamics. We argue that electrons accumulating in states degenerate with the M valley could travel through a multilayer flake of InSe with a lateral size of 1 μm. 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 transition and many-body screening of the Froehlich coupling.

2. Low-dimensional materials

Valerie Smejkal (Contributed)

Simulation of the Ultrafast Exciton Buildup in Monolayer MoS_2

The optical spectra of monolayer transition metal dichalcogenides (TMDs) are strongly dom- inated by excitonic peaks in the visible range. The cause for this is the reduced screening and thus enhanced Coulomb interaction in these monolayers leading to strongly bound electron- hole pairs with binding energies of the order of hundreds of meV.
While the exciton, charge and spin relaxation dynamics in these materials have been studied extensively fewer publications discuss the exciton formation dynamics [1,2].

We study the exciton formation dynamics in MoS_2 from first-principles by the time evolution of the density matrix including electron and hole correlations and the interaction with time-dependent external fields [3]. The system is pumped (see Fig.1) by short (20 fs) laser pulses with energies between the A-excitonic resonance (1.9 eV) and energies far in the con- duction band (3.4 eV). While the A-exciton buildup is expected to be instantaneous, different mechanisms play a role when carriers are excited above the band gap. They first have to relax from the quasi-free electron-hole plasma above the band gap to the excitonic ground state via scattering by phonons, electrons or excitons.
By inclusion of electron-phonon scattering matrix elements from first principles we elucidate the role of this scattering channel for the relaxation. Comparison with recent experiments allows for an assessment of the theoretical assumptions.
References

[1] F. Ceballos, et al., Nanoscale 8, 11681-11688 (2016).
[2] C. Trovatello, et al., CLEO: QELS_Fundamental Science, Optical Society of America (2018).
[3] A. Marini, J. Phys.: Conf. Ser. 427, 012003 (2013).

Stefano Calati (Contributed)

Dynamic Screening of Quasiparticles in WS_2 Monolayers

The low dimensional nature of transition metal dichalcogenides (TMDCs) and the resulting reduced screening significantly influence their non-equilibrium optical properties, as dynamic screening by photoexcited quasiparticles governs the transient response.

In this work, we investigate the role of different photoexcited quasiparticles on the dynamic response of WS_2 monolayers on SiO_2: excitons generated by resonant pumping and quasi-free carriers photoexcited by above-resonance pumping. Drastic changes in the reflectivity contrast upon photoexcitation are observed in both cases and the contributions to the neutral exciton and the trion are isolated. The main observation is a pump photon energy-dependent blue/red shift of the neutral exciton for resonant/above-resonance pumping, respectively. Both, photoexcited excitons and quasi-free carriers screen the Coulomb interaction, leading to a weaker/stronger renormalization of the quasi-free-particle band gap compared to the dynamic screening-induced reduction of the exciton binding energy. The relative interplay between these two effects explains the observed blue/red shift crossover. Using a simple rate equation model, it is possible to, for instance, extract exciton formation and decay times from the multiexponential dynamics of the exciton and trion resonances.

5. Theoretical and computational methods for systems out of equilibrium

Irene Burghardt (Keynote)

Ultrafast Quantum Dynamics of Functional Organic Polymer Materials: Coherence, Confinement, and Disorder

This talk addresses quantum dynamical studies of ultrafast photo-induced energy and charge transfer in functional organic materials, complementing time-resolved spectroscopic observations that un- derscore the coherent nature of the ultrafast elementary transfer events in these molecular aggregate systems [1]. The intricate interplay of electronic delocalization, coherent vibronic dynamics, and trapping phenomena requires a quantum dynamical treatment that goes beyond conventional mixed quantum-classical simulations. Our approach combines first-principles parametrized Hamiltonians [2], with accurate quantum dynamics simulations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method [3] and its multi-layer

(ML-MCTDH) variant [4], along with semiclas- sical approaches [5]. This talk will specifically focus on (i) exciton dissociation and free carrier generation in regioregular donor-acceptor assemblies [2,6], and (ii) the elementary mechanism of exciton migration [5,7,8] and creation of charge-transfer excitons [9] in polythiophene type donor materials. Special emphasis is placed on the influence of structural and dynamic disorder and molec- ular packing, which can act as a determining factor in transfer efficiencies. Against this background, we will comment on the role of temporal and spatial coherence along with a consistent description of the transition to a classical-statistical regime.

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Davide Sangalli (invited)

ab-initio description of pump and probe experiments: from carriers to exciton dynamics

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 extendend 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 excitonc resonances [1] and the physics of excitons [7-9]. 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 exciton dynamics and their signature in photoemission [8-9].

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Simone Latini (invited)

Sangeeta Sharma (invited)

Sivan Refaely-Abramson (Contributed)

New Insights into complex exciton phenomena in materials from many-body perturbation theory

Theoretical predictions of excited-state phenomena in complex materials can lead to better understanding of nanoscale energy conversion mechanisms, for instance in emerging photovoltaic and photocatalytic systems. In this talk I will discuss recent studies using new ab initio many-body perturbation theory methods within the GW approximation and the Bethe Salpeter equation approach (GW-BSE) to understand and uncover such mechanisms. In one example, I will present a new approach to calculate multi-exciton generation processes in solids from first principles, used to study singlet fission in organic crystals. Applying this approach to crystalline pentacene, we

discovered a new exciton—bi-exciton coupling channel, one that is purely Coulombic, with a predicted decay rate comparable to experiments; our results suggest new understanding of the role of symmetry and structure in the singlet fission mechanism in the solid state. Additionally, I will discuss recent GW-BSE calculations of excited state properties in monolayer transition metal dichalcogenides with point defects. These impurities give rise to localized states, introduce strongly-bound excitons below the absorption edge, and reduce the valley-selective circular dichroism, suggesting a novel pathway to tune spin-valley polarization and other optical properties through defect engineering.

6. Attosecond dynamics in molecules and nanostructures (II)

Ivano Tavernelli (Keynote)

Fernando Martin (invited)

Attosecond pump-probe spectroscopy of molecular electron dynamics: a theoretical point of view

Attosecond and few femtosecond light pulses allow one to probe the inner workings of atoms, molecules and solids on the timescale of the electronic motion. In molecules, sudden ionization by such pulses is followed by charge redistribution on a time scale ranging from a few-femtoseconds down to hundreds attoseconds, and usually leads to fragmentation of the remaining molecular cation. Such complex dynamics arises from the coherent superposition of electronic states populated by the broadband attosecond pulse and from rearrangements in the electronic structure of the molecular cation due to electron correlation. To investigate these ultrafast processes, attosecond pump-probe spectroscopy has been shown to be a very valuable tool. In this talk I will present the results of recent attosecond pump-probe simulations in which several atoms and molecules, from hydrogen to the amino acid tryptophan, are ionized with a single or a train of attosecond pulses and are subsequently probed by an infrared or an XUV pulse (see [1] for a recent review on the subject).

[1] M. Nisoli, P. Decleva, F. Calegari, A. Palacios, and F. Martín, Chem. Rev. 117, 10760 (2017).

Aaron Kelly (invited)

Trajectory-based Approaches to Quantum Dynamics: Wavefunctions, Density Matrices, and Master Equations

I will present recently developed trajectory-based approaches for treating nonequilibrium quantum dynamics in molecular and condensed phase systems. Rooted in mean field

theory, these methods employ statistical ensembles of trajectories to simulate the real-time dynamics of nonadiabatic processes like charge and energy transfer. We will explore the performance of selected techniques of this type in a variety of scenarios, including proton-coupled electron transfer reactions, exciton dissociation and charge separation at heterojunction interfaces, and the relaxation of photo-generated charge carriers in molecular wires.

Christian Schaefer (invited)

Ab initio cavity QED - dipping the toe into cavity chemistry

The alchemical dream of altering a given material on demand into something desirable is at the very heart of chemistry and the control by slow down, acceleration or steering a reaction can render existing pathways far more beneficial or even open new ones. With the field of cavity QED, a completely novel approach has emerged that calls for theoretical foundations. Quantum electrodynamical density functional theory in conjecture with adjusted wavefunction approaches such as the cavity Born-Oppenheimer technique provide a possibility to predict from first-principles how non-intrusive steering of chemical reactions in cavity QED can take place. Applying it to recent experiments, we will present the methodology that allows us to gather so far unavailable insight together with first conclusions about the forces that drive cavity QED.

Peter Saalfrank (Contributed)

Correlated wavefunction approaches to laser-driven electron dynamics in molecules and their control

Recent progress in generating intense laser fields, has pushed the timescale for probing dynamical processes in atomic and molecular systems down to the attosecond domain (1 as=10−18 s). In parallel with experiments, which are more and more applied to molecular systems, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes our efforts to extend ab initio wavefunction based methods of stationary electronic structure theory, to the explicitly time-dependent domain, and their application to molecular systems. In particular, time-dependent configuration interaction (TD-CI) [1] and time-dependent complete active space SCF methods (TD-CASSCF) [2] will be introduced as systematically improvable, correlated methods for propagating electronic wavefunctions in real time. Extensions towards the treatment of ionization, dissipation, and nuclear motion will be discussed briefly.

Armed with these methods, we seek to describe electronic motion in laser-driven molecular systems, and to control it at will, using shaped, ultrashort laser pulses. In one example, we shall describe High Harmonic Generation (HHG) spectra of molecules with the following purposes: to study the effects of ionization, nuclear motion, and rotational

orientation of diatomic and triatomic molecules on HHG spectra [3, 4]; to control HHG by stochastic pulse optimization [5]; and, finally, to distinguish polyatomic organic isomers by their HHG spectra [4]. In a second set of examples we try to enforce selective state-to-state transitions or the creation of specific electronic wavepackets, e.g., as a hitherto purely theoretical concept – a Hartree-Fock state by optimal control theory starting from the (correlated) ground state of an atom or molecule [6].

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[5] J.B. Schönborn, P. Saalfrank, and T. Klamroth, J. Chem. Phys. 144, 044301 (2018).
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7. Natural and artificial light harvesting

Alexandra Olaya-Castro

Erling Thyrhaug (invited)

Joel Yuen-Zhou (invited)

Vasil Rokaj (Contributed)

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

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.

[1] V. Rokaj, M. Penz, M. Sentef, M. Ruggenthaler, and A. Rubio, Phys. Rev. Lett. 123, 047202 (2019)

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