

Internationalen CECAM-Workshop

Charge carrier dynamics in nanostructures: *optoelectronic and photo-stimulated processes*

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Organizers

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Date and Venue

Workshop, 9th – 13th October 2017, Bremen, Germany

Motivation

Advances of time-resolved experimental techniques, needed for a detailed understanding of charge carrier dynamics as they occur in real time, require matching progress in theoretical approaches. Applications to novel, emerging nanoscale materials, which ultimately lead to faster, more efficient and miniaturized devices, pose multiple theoretical challenges. Modeling time-resolved experimental data becomes a major goal of a theorist.

The proposed workshop should become a forum to brainstorm ideas about solutions to important computational problems, and identify new directions for time-dependant electronic structure method development and challenging applications. In this way, we hope to create an exchange mechanism to unite a core of developers in an interactive environment, in order to initiate design of a new generation software tools for quantum modelling of realistic complex systems and nanostructures in electronic ground and excited states. The delivery of this technology to a broad community would facilitate breakthroughs on high-impact materials science problems.

Computational materials sciences are outstanding growth areas of research. In the future, an increasingly larger part of our technological development will depend on computer applications, in particular in materials, nano and bio-nano sciences. *Ab initio* calculations based on the density functional theory, in combination with the time-dependant extensions, can make a

considerable progress in the field. Such calculations can guide design of a variety of materials, for instance for solar energy applications, increasing the photo-catalytic yield and the conversion efficiency of light into electricity. Furthermore, the non-equilibrium processes involved in the photo-induced charge separation and transport require explicit time domain modelling, in direct comparison with advanced time-resolved experimental techniques.

State of the art

Experiment

On the experimental side, there has been intensive effort in the advancement of time-resolved experimental techniques probing the transient electronic structure after excitation of charge carriers with light or intense pulsed laser fields. E.g., this includes the study of resonant energy transfer of triplet excitons from pentacene to lead selenide (PbSe) nanocrystals, where Akshay et al. [1] report on efficient resonant-energy transfer of molecular spin-triplet excitons from organic semiconductors to inorganic semiconductors. They use ultrafast optical absorption spectroscopy to track the dynamics of triplets, generated in pentacene through singlet exciton fission, at the interface with PbSe nanocrystals.

The direct imaging of microscopic structural changes on ultrafast timescales is a particular challenge in the natural sciences. Alongside ultrafast X-ray techniques, time-resolved electron microscopy, diffraction and spectroscopy will yield unprecedented insights into rapid physical, chemical and biological processes. Various authors in most recent years follow a variety of imaging approaches with ultrashort, highly coherent electron pulses to investigate the dynamics of ultrafast electronic and structural phenomena. Over the past few years, Feist and Schäfer et al. [2] have developed a novel implementation of Ultrafast Transmission Electron Microscopy ("UTEM"). The instrument employs a "pump-probe" scheme, in which two laser pulses are coupled into the column of a transmission electron microscope (TEM). A first laser pulse excites an electronic or structural change in the investigated sample. In a special photocathode, a second, delayed laser pulse generates an ultrafast electron pulse, which then probes the induced sample change in microscopy, diffraction or spectroscopy. By varying the relative pulse delay, the dynamics can be followed in time.

Transition metal dichalcogenides (TMDs) are emerging as promising two-dimensional (2D) semiconductors for flexible optoelectronic, spintronic and photovoltaic devices. Their photophysical properties are of pivotal importance for the understanding and optimization of device operation; however, A microscopic explanation of the photophysics is still lacking. Cerullo and Pogna et al. [3] use femtosecond transient absorption spectroscopy, with pump pulse tunability and broadband probing, to monitor the relaxation dynamics of single-layer MoS₂ over the entire visible range, upon photoexcitation of different excitonic transitions. They find that, irrespective of excitation photon energy, the transient absorption spectrum shows simultaneous bleaching of all excitonic transitions and corresponding red-shifted photoinduced absorption bands. First-principle modeling of the ultrafast optical response reveals that a transient bandgap renormalization, caused by the presence of photoexcited carriers, is primarily responsible for the observed features.

Multi-dimensional ultrafast pulsed coherent optical spectroscopy is used to understand and control light-matter interactions in semiconductor nanostructures, see, Nardin and Cundiff et al. [4] and in photo-synthetic biological architectures. In oxygenic photosynthesis, the initial charge separation occurs in the photosystem II reaction centre, the only known natural enzyme that uses solar energy to split water. Both energy transfer and charge separation in photosynthesis are rapid events with high quantum efficiencies. In recent nonlinear spectroscopic experiments, long-lived coherences have been observed in photosynthetic antenna complexes, and theoretical work suggests that they reflect underlying electronic–vibrational resonances, which may play a functional role in enhancing energy transfer. Using two-dimensional electronic spectroscopy, Fuller and Ogilvie et al. [5] report the observation of coherent dynamics persisting on a picosecond timescale at 77 K in the photosystem II reaction centre.

Coherent multidimensional electronic spectroscopy can be employed as well to unravel various channels in molecular chemical reactions. This approach is thus not limited to analysis of energy transfer or charge transfer (i.e. processes from photophysics), but it can also be employed in situations where the investigated system undergoes permanent structural changes (i.e. in photochemistry), see Nuernberger and Brixner et al. [6]. Kolano and Hamm et al. [7] recently introduced the method of transient 2D-IR spectroscopy, which extends conventional 2D-IR spectroscopy to the non-equilibrium regime, allowing one to make 'molecular movies' of fast conformational changes in proteins and “watch hydrogen-bond dynamics”.

Coherent vibrational motion of molecular moieties can be monitored experimentally, e.g. motion of fullerenes after ultra-short impulsive optical excitation of the polymer donor [8]. Comparison with first-principle theoretical simulations evidenced coherent electron transfer between donor and acceptor, and oscillations of the transferred charge with a 25-femtosecond period matching that of the observed vibrational modes. The results show that coherent vibronic coupling between electronic and nuclear degrees of freedom is of key importance in triggering charge delocalization and transfer in a noncovalently bound reference system.

Adaptive shaping of the phase and amplitude of femtosecond laser pulses has been developed recently into an efficient tool for the directed manipulation of interference phenomena, thus providing coherent control over various quantum-mechanical systems [9]. This experimental realization opens a number of perspectives in coherent control, nano-optics, nonlinear spectroscopy, and other research fields in which optical investigations are carried out with spatial or temporal resolution. Other time resolved techniques include attosecond spectroscopy to unravel charge migration and dynamics in organic materials, Kraus and Woerner et al. [10]. Calegari et al. report the application of isolated attosecond pulses to prompt ionization of the amino acid phenylalanine and the subsequent detection of ultrafast dynamics on a sub-4.5-femtosecond temporal scale, which is shorter than the vibrational response of the molecule. The ability to initiate and observe such electronic dynamics in polyatomic molecules represents a crucial step forward in attosecond science, which is progressively moving toward the investigation of more and more complex systems [11].

Summarizing, the advancement of time-resolved experimental techniques described above strongly demands to simultaneously advance the computational approaches to accurately model respective processes and understand the charge carrier dynamics and related transient phenomena on a fundamental level.

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- [6] P. Nuernberger, T. B. et al. Angew. Chemie – International Edition 54, (2015) 11368
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- [8] S. M. Fa, A. Rubio, E. Molinari, Christoph Lienau, Science 344 (2014) 1001
- [9] M. Aeschlimann et al. Nature 446 (2007) 301
- [10] P. M. Kraus, H. J. W., et al Science 350 (2015) 790
- [11] F. Calegari et al. Science 346 (2014) 346

Theory

Theoretical studies on photo-physical and photochemical processes in nanoscale systems have been widely developed in the decades and will continue to be a topic of interest in forefronts of natural science. In addition to experimental science, computational modelling can give important information and help us to understand different issues at molecular, atomic and even electronic levels of detail

Recent progress in electron-nuclear dynamics enable numerical simulations of complex ultrafast processes in the condensed phase. These advances have opened new avenues in the study of various photo-physical and photochemical processes triggered by the interaction with electromagnetic radiation. In particular, theoretical investigations can be combined with the most sophisticated femtosecond experimental techniques to guide the interpretation of measured time-resolved observables. At the same time, the availability of experimental data at high resolution, in both space and time, offers a unique opportunity for the benchmarking and improvement of the theoretical models used to describe complex molecular systems in their natural environment. The established synergy between theory and experiments can produce a better understanding of the ultrafast physical and chemical processes at the atomistic scale resolution. Furthermore, reliable *ab initio* molecular dynamics simulations can already be successful to predict and guide new experiments, as well as to design novel and more efficient materials. The aim is to describe the system of interest under the most realistic ambient conditions including all environmental effects that influence experiments, for instance, the interaction with the solvent and with an external time-dependent electric field. To this end, time-dependent density functional theory (TD-DFT) is among the most efficient and accurate methods for the representation of the electronic dynamics, while nuclei move classically on the potential surface provided by the electrons. The semi-classical and mixed quantum-classical approaches include Tully's surface hopping [1] and the mean-field non-adiabatic Ehrenfest

dynamics [2,3]. Various groups have successfully applied these methods to investigate solar cells [4], plasmonic nanoparticles [5], chemical reactions and other processes

Theoretical studies of charge transport in nanoscale systems provide profound insights into the non-equilibrium processes involved in the photo-induced charge separation and migration. While the combined density functional theory (DFT) and non-equilibrium Green's function (NEGF) approach has been widely employed to simulate steady state quantum electron transport through molecular junctions and other nanoscopic structures, the photo-induced processes require explicit time-domain simulations for direct comparison with advanced time-resolved experimental techniques. TD-DFT has been developed to study quantum transport phenomena [6-7]. As a formally rigorous and numerically tractable approach, TD-DFT promises real-time simulations on ultrafast electron transport through realistic electronic devices. By employing the NEGF approach and a partition-free scheme, Kurth, *et al.* derived the exact equations of motion for the two-time Green's functions within TDDFT framework. They proposed a practical scheme in which the electronic wave-function is propagated in time domain that is subject to open boundaries [6]. The resulting numerical method has been tested on model systems. Based on a reduced single-electron density matrix formulation, Zheng, *et al.* derived TD-DFT equations for open systems and applied them to realistic problems [7].

To cope with the increasing demand for renewable energy supply, solar cell research has become a hot topic within science and engineering. The need for higher solar cell efficiencies at a lower cost has become apparent. At the same time, synthetic control in nanoscience has improved such that high-performance electronic devices are now becoming possible. Nanowire solar cells have some potential benefits over traditional wafer-based or thin-film devices. Functioning nanowire photovoltaics have been fabricated using a wide variety of materials. Output efficiencies have steadily increased and have now achieved efficiencies close to 10%. At the same time, a number of unresolved questions must be answered before such materials can be used in commercial devices. Based on the NEGF formalism, Zhang, *et al.* modeled quantum mechanically the full I-V characteristics of a nanowire-based photovoltaic device [8]. Organic photovoltaics show great promise owing to their synthetic variability, low temperature processing, and the possibility of producing lightweight, flexible, easily manufactured and inexpensive devices. However, the detailed mechanism of formation and dissociation of the charge transfer (CT) states is still controversial. Recently, a combined spectroscopic and non-adiabatic Ehrenfest dynamics study demonstrated a coherent ultrafast electron transfer between donor and acceptor in a prototype organic photovoltaic device [9].

Surface plasmons are collective oscillations of electrons that couple to electromagnetic fields, support intense electromagnetic field concentrations, and provide a pathway to couple optical energy from free space in nanoscale systems. Plasmons can decay either radiatively via emission of photons or non-radiatively through generation of excited carriers, referred to as hot carriers. Decay of surface plasmons to hot carriers finds a wide variety of applications in energy conversion, photocatalysis and photodetection. However, existing models fail to explain key quantitative details of the conversion of plasmons to hot carriers observed in experiments. Based on Fermi Golden's rule and DFT calculations, Sundararaman, *et al.* report predictions for the prompt distributions of hot carriers generated by plasmon decay and find that carrier energy distributions are sensitive to the electronic band structure of the metal [10]. Bernardi, *et al.*

combine DFT, GW and electron phonon calculations to study the energy distribution and scattering processes for hot carriers generated by surface plasmons in noble metals. The calculations predict optimal conditions for hot carriers generation and extraction [11].

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Objectives

The proposed workshop should become a forum to discuss experimental and computational progress, and to generate a unified understanding of charge carrier dynamics in nanostructures and at interfaces. We are aiming to achieve the following key objectives:

- Bring together researchers from experiment and theory working on time-dependent charge carrier dynamics related to optoelectronic and photo-stimulated processes, in order to highlight recent progress, and to discuss challenges and opportunities in the materials aspect of tailor-made nanostructures and hybrid interfaces for highly efficient energy applications.
- Foster the exchange of methodological expertise and new developments between scientists working on different aspects of charge dynamics at surfaces, interfaces, and in 2D-materials and hetero-structures.
- Discuss possibilities for optimizing the materials properties and device design. The interdisciplinary character of the workshop will help finding solutions for overcoming current limitations.

- Provide opportunity to form new worldwide interdisciplinary collaborations on time-dependent spectroscopy for the mutual benefit of theoretical, experimental and applied researchers.

Tentative list of invited speakers

Experimental studies

Akshay Rao, Cavendish Laboratory Cambridge, **organic photovoltaics**, ar525@cam.ac.uk

Sascha Schäfer University Goettingen, **ultrafast electron microscopy**,
schaefer@ph4.physik.uni-goettingen.de

Gulio Cerullo, Politecnico di Milano, **ultrafast optical 2D spectroscopy**, giulio.cerullo@polimi.it

Jeniffer Ogilvie, University of Michigan Ann Arbor, **exciton dynamics in light-harvesting complexes**, jogilvie@umich.edu

Steven Cundiff, University of Michigan Ann Arbor, **light-matter interactions in semiconductors**,
cundiff@umich.edu

Tobias Brixner, University of Wuerzburg, **multi-dimensional spectroscopy of molecular processes**, brixner@phys-chemie.uni-wuerzburg.de

Francesca Calegari, MPI-SDM Hamburg, Politecnico di Milano, **ultra-fast charge carrier dynamics**, francesca.calegari@polimi.it

Rupert Huber, University of Regensburg, **Terahertz control of electronic processes**,
rupert.huber@physik.uni-regensburg.de

Tenio Popmintshev, JILA and University of Boulder (San Diego), **Attosecond x-rays**,
popmintshev@jila.colorado.edu

Christoph Lienau, University of Oldenburg, **Ultra-fast nano-optics**, christoph.lienau@uni-oldenburg.de

Hans-Jakob Woerner, ETH-Zuerich, **Attosecond spectroscopy in molecular systems and solutions**, hansjakob.woerner@phys.chem.ethz.ch

Peter Hamm, University of Zuerich, **2D-spectroscopy in biosystems**, peter.hamm@chem.uzh.ch

Alfred Leitenstorfer, University of Konstanz, **Terahertz-spectroscopy of solids/nanostructures**,
alfred.leitenstorfer@uni-konstanz.de

Jascha Repp, University of Regensburg, **time-resolved scanning tunnelim microscopy**,
Jascha.Repp@physik.uni-regensburg.de

Martin Aeschlimann, University of Kaiserslautern, **Ultrafast surface phenomena**,
ma@physik.uni-kl.de

Greg Scholes, Princeton University, Ultrafast spectroscopy of biological and inorganic light-harvesting systems, gscholes@princeton.edu

Computational approaches and applications

Ravishankar Sundararaman, Rensselaer Polytechnic Institute, Hot electrons in nanoplasmonics, shankars@caltech.edu

Marco Bernardi, Caltech Pasadena, Exciton dynamics in TMDs from many-body perturbation theory, bmarco@caltech.edu

Andrew Horsfield, Imperial College London, Nanowires for photovoltaics, a.horsfield@imperial.ac.uk

Yosuke Kanai, University of North-Carolina, Chapel Hill, electron transfer at interfaces, ykanai@unc.edu

Elisa Molinari, University of Modena, organic photovoltaics, elisa.molinari@unimore.it

Chi Yung Yam, Beijing Comp. Sci. Res. Center, photovoltaic and optoelectronic devices, yamcy@csrc.ac.cn

Sheng Meng, Institute of Physics, CAS Beijing, Dye-TiO₂, excitonic solar cells, TDDFT, smeng@iphy.ac.cn

Guanhua Chen, University of Hongkong, TDDFT, solar cell devices, ghc@everest.hku.hk

Oleg Prezhdo, University of Southern California, Los Angeles, solar cells, NAMD, PYXAID, prezhdo@usc.edu

Thomas Niehaus, University of Lyon, TD-DFTB, thomas.niehaus@univ-lyon1.fr

Steven Louie, University of California, Berkeley, GW and beyond, 2D materials, TMDCs, sglouie@berkeley.edu

Johannes Lischner, Imperial College London, nanoplasmonics, jlischner597@gmail.com

Sergei Tretiak, Los Alamos National Laboratory, organic solar cells NAMD, serg@lanl.gov

Hardy Gross, MPI-Halle, control of electron dynamics, hardy@mpi-halle.mpg.de

Shaul Mukhameh, University of California, Irvine, multi-dimensional optical spectroscopy (bio and semiconductors), smukamel@uci.edu

Jochen Blumberger, University College London, Electron transport/transfer in organic and biological structures, j.blumberger@ucl.ac.uk

Enrico Perfetto, University Tor Vergata Rome, 1st principle NEGF time-resolved photoabsorption, enrico.perfetto@roma2.infn.it

Heiko Appel, MPI-SDM Hamburg, Light-matter coupling in density-functional theory for quantum electrodynamics, appel@fhi-berlin.mpg.de

Ivano Tavernelli, IBM Research Laboratory Zurich, TDDFT-based nonadiabatic Quantum Dynamics with Trajectories, ITA@zurich.ibm.com

Andrea Carlo Rozzi, Institute for Nanoscience, Modena, charge separation in light-harvesting materials, carloandrea.rozzi@nano.cnr.it

Irene Burghardt, University of Frankfurt, photo-physics of functional organic polymer materials, burghardt@chemie.uni-frankfurt.de

Christian Sanchez, University of Cordoba, light driven nanomotors, NAMD-DFTB, cristian.g.sanchez@gmail.com

Ignacio Franco, University of Rochester, Laser control of electronic properties and dynamics franco@chem.rochester.edu