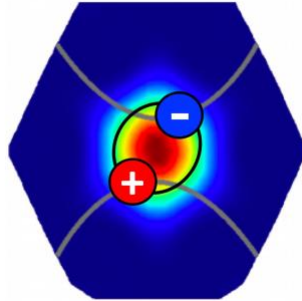


Exciton dynamics in functional materials: new theoretical frontiers



*December 13 - 16, 2021
On-line, hosted by CECAM-HQ-EPFL*

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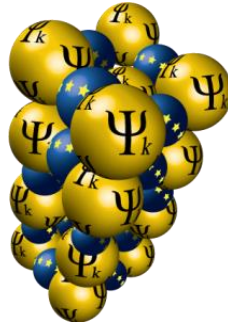
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With the support of:



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1. Description

Electronic and optical interactions dominate emerging applications, including optimizing solar energy conversion and storage, producing tunable light-emitting diodes, designing photon emitters for quantum information science, and more. The involved processes typically include energetically-excited states, and in particular, neutral or charged energy carriers called *excitons*, composed of excited electrons and holes, bound together through Coulomb interaction. The exciton relaxation, scattering, and decay dynamics, as well as their ballistic and diffusive transport, are key ingredients in device functionality and are closely related to the atomic composition of the materials and the selection rules resulting from it. Understanding the relation between material structure and excited-state properties as well as their dynamics is hence of great interest. It can introduce design pathways to control and tune underlying interaction mechanisms in broad areas of photophysics.

In recent years, extensive experimental research is dedicated to studying time-resolved excited-state phenomena in solid-state functional materials, such as monolayer transition metal dichalcogenides (TMDCs), organic molecular crystals, organic-inorganic hybrids, quantum dot solids, and metal-organic complexes. Such systems often host strongly-bound excitons as energy carriers, typically with exciton binding energies of tens to many hundreds of meV. Advanced time-resolved spectroscopy and microscopy experiments suggest that those excitons can exhibit a rich variety of dynamics due to a number of complex phenomena. These include nonradiative multi-exciton generation in organic crystals, Auger recombination and exciton-exciton annihilation in 2D materials, and the decay of bright excitons into low-lying dark states constrained by momentum in valley-selective monolayers or quantum dots. Complex interaction processes are further shown to have strong coupling to phonons and structural inhomogeneities, such as atomic defects, local strain, or environmental screening. The goal of this workshop is to bring together researchers from different scientific communities, who study time-resolved exciton phenomena in functional materials using a broad variety of approaches. While the main focus of the workshop is computational developments, an important aspect of it is a state-of-the-art experimental perspective. Within a joint cross-community computational-experimental meeting, we wish to encourage exchange of ideas and identify emerging questions for future research directions and collaborations, as well as to share and advance current theoretical methods to exciton dynamics and transport in functional materials.

2. Program

Day 1 - Monday December 13th 2021

Opening remarks 12:45 to 13:00

Session 1, chair: Sivan Refaely-Abramson 13:00 to 15:50

- 13:00 to 13:25 - **Lorenzo Maserati**
2D excitons in self-assembled metal organic chalcogenides quantum wells
- 13:25 to 13:50 - **Aaron Kelly**
Simulating exciton transport in molecular aggregates with quantum-classical mapping methods
- 13:50 to 14:15 - **Malte Rösner**
Exciton and plasmon trapping via spatial coulomb engineering in layered materials
- 14:15 to 14:35 – Break
- 14:35 to 15:00 - **Paulina Plochocka**
Excitons and phonons in 2D perovskites
- 15:00 to 15:25 - **Andreas Knorr**
Ultrafast transfer processes and exciton-exciton interactions in (functionalized) atomically thin semiconductors
- 15:25 to 15:50 - **Marina Filip**
Phonon screening of excitons in lead-halide perovskite semiconductors and beyond
- 15:50 to 16:10 - Break

Session 2, chair: Alexey Chernikov 16:10 to 19:00

- 16:10 to 16:35 - **Hadar Steinberg**
Spectroscopy and charge sensing using defects in van der Waals layers
- 16:35 to 17:00 - **Ting Cao**
Theory of excitons in 2D magnet materials - interlayer interactions and entanglement
- 17:00 to 17:25 - **Dongbin Shin**
Simulating THz field-induced ferroelectricity in quantum paraelectric SrTiO₃
- 17:25 to 17:45 – Break
- 17:45 to 18:10 - **Xavier Marie**
Exciton dynamics in atomically thin transition metal dichalcogenides
- 18:10 to 18:35 - **Mikhail Glazov**
Quantum transport of excitons in 2D semiconductors
- 18:35 to 19:00 - **Andrés Montoya-Castillo**
Optical spectroscopy in the condensed phase: how to capture disorder, anharmonicity, & dynamical effects

Day summary and discussion 19:00 to 19:30

Day 2 - Tuesday December 14th 2021

Session 3, chairs: Felipe Jornada, Archana Raja 13:00 to 17:25

- 13:00 to 13:25 - **Akshay Rao**
Tracking exciton dynamics in time and space with sub-10fs time-resolution and sub-10nm spatial precision
- 13:25 to 13:50 - **David Egger**
Interrelations of lattice vibrations and optoelectronic properties in halide perovskites
- 13:50 to 14:15 - **Simone Latini**
Designing quasi-particles of light and photo-groundstates
- 14:15 to 14:35 – Break
- 14:35 to 15:00 - **Ronen Rapaport**
Strong interactions in correlated dipolar quantum fluids of excitons and polaritons
- 15:00 to 15:25 - **Alexander Steinhoff**
Microscopic theory of exciton-exciton annihilation in two-dimensional semiconductors
- 15:25 to 15:50 - **Roel Tempelaar**
Towards mixed quantum-classical simulations of nonequilibrium phenomena in bulk and low-dimensional materials
- 15:50 to 16:10 – Break
- 16:10 to 16:35 - **Stephan Kuemmel**
Revealing electron dynamics in real time with time-dependent density functional theory
- 16:35 to 17:00 - **Gabriel Antonius**
Theory of the exciton-phonon coupling
- 17:00 to 17:25 - **Benjamin Levine**
Nonradiative recombination and hot carrier cooling through conical intersections

Day summary and discussion 17:25 to 17:55

Online poster session, online beer (self-served) 18:00 to 19:00

Day 3 - Wednesday December 15th 2021

Session 4, chair: Angel Rubio, Alexey Chernikov 13:00 to 15:50

- 13:00 to 13:25 - **Andras Kis**
Exciton manipulation and transport in 2D semiconductor heterostructures
- 13:25 to 13:50 - **Vladimir Falko**
 Γ -to- Γ optical transitions in van der Waals heterostructures of 2D materials
- 13:50 to 14:15 - **Manish Jain**
Ab initio calculation of moiré excitons in twisted MoS₂/MoSe₂ heterostructures

- 14:15 to 14:35 – Break
- 14:35 to 15:00 - **Keshav Dani**
Exploring excitonic excitations through their momentum coordinates
- 15:00 to 15:25 - **Davide Sangalli**
Ab initio approach to exciton dynamics
- 15:25 to 15:50 - **Dante Kennes**
Moiré heterostructures: a condensed matter quantum simulator
- 15:50 to 16:10 - Break

Session 5, chair: Timothy Berkelbach 16:10 to 19:00

- 16:10 to 16:35 - **Libai Huang**
Spatial and temporal imaging of exciton transport in two-dimensional heterostructures
- 16:35 to 17:00 - **Ermin Malic**
Exciton optics, dynamics and transport in atomically thin materials
- 17:00 to 17:25 - **Diana Qiu**
Exploring many-body effects on the dynamics of optical excitations in low-dimensional materials
- 17:25 to 17:45 – Break
- 17:45 to 18:10 - **Milan Delor**
TBA
- 18:10 to 18:35 - **Sahar Sharifzadeh**
Applying the special displacement method to understand exciton-phonon interactions in 2D materials
- 18:35 to 19:00 - **Antonios Alvertis**
Impact of strong exciton-phonon interactions and anharmonicity on the optoelectronic properties of organic semiconductors

Day summary and discussion 19:00 to 19:30

Day 4 - Thursday December 16th 2021

Session 6, chair: Sivan Refaely-Abramson, Angel Rubio 13:00 to 17:25

- 13:00 to 13:25 - **Kaiqiang Lin**
Narrowband high-lying excitons in transition metal dichalcogenide monolayers and bilayers
- 13:25 to 13:50 - **Malte Selig**
Correlated phases in TMDC heterostructures
- 13:50 to 14:15 - **Kristian Thygesen**
Excitons and quantum light-matter interactions in 2D materials
- 14:15 to 14:35 – Break

- 14:35 to 15:00 - **Dan Oron**
Heralded spectroscopy of quantum confined nanoscale emitters
- 15:00 to 15:25 - **Annika Bande**
Atomistic simulations of laser-controlled exciton transfer and stabilization in symmetric double quantum dots
- 15:25 to 15:50 - **Felix Plasser**
Detailed insight into exciton wavefunctions from quantum chemistry computations
- 15:50 to 16:10 – Break
- 16:10 to 16:35 - **Jonah Haber**
Tba
- 16:35 to 17:00 - **Enrico Perfetto**
Dynamics of coherent excitons in resonantly excited semiconductors
- 17:00 to 17:25 - **Feliciano Giustino**
Phonon-driven Rashba-Dresselhaus effect

Day summary and discussion 17:25 to 17:55

Concluding 17:55 to 18:00

3. Abstracts

2D excitons in self-assembled metal organic chalcogenides quantum wells

Lorenzo Maserati

Istituto Italiano di Tecnologia, Milano, Italy

I will present spectroscopic studies in a new material platform based on layered organic metal-chalcogenides, more robust and easily accessible than 2D perovskites, reminiscent of 2D transition metal dichalcogenides. The material tunable excitonic properties allows to access different energy scales and testing correlated many-body phenomena. Our recent experimental work supported by GW-BSE calculations [1] and a study lead by Shuck group at Columbia University [2] demonstrated that layered metal organic chalcogenides host two-dimensional, room temperature stable anisotropic excitons. Moreover, I will show that in the [AgSePh]_n system, exciton self-trapping causes a complete and highly effective material de-excitation within a few picoseconds. While fast trapping is often considered detrimental in the context of energy conversion, where charge carriers need to be collected within their lifetime, it opens new possibilities in technologically compelling field of ultrafast photonic switches.

[1] L. Maserati, S. Refaely-Abramson, C. Kastl, C. Chen, N. Borys, C. Eisler, M. Collins, T. Smidt, E. Barnard, M. Strasbourg, E. Schriber, B. Shevitski, K. Yao, J. Hohman, P. Schuck, S. Aloni, J. Neaton, A. Schwartzberg, *Mater. Horiz.*, **8**, 197 (2021)

[2] K. Yao, M. Collins, K. Nell, E. Barnard, N. Borys, T. Kuykendall, J. Hohman, P. Schuck, *ACS Nano*, **15**, 4085 (2020)

Ab initio approach to exciton dynamics

Davide Sangalli

Consiglio Nazionale delle Ricerche, Italy

In this talk I present a fully abinitio approach to model the generation of non-equilibrium coherent excitonic states with ultra-short laser pulses. The modelling is achieved via the real-time propagation of the density matrix projected in the Kohn-Sham basis set, within the time-dependent Hartree plus Screened EXchange (TD-HSEX) approximation [1]. I show how the generated density matrix can be used to model transient spectroscopy signals in the presence of strongly bound excitons. Using LiF as a prototype material, I show that the scheme is able to capture the exciton signature both in time-resolved angle-resolved photoemission spectroscopy and transient absorption experiments [2, 3]. The approach is completely general and can become the reference scheme for modeling pump and probe experiment in a wide range of materials. Finally, I discuss how the generated coherent excitonic states can be related to non-coherent states with a thermal distribution of excitons, and how to compute their lifetimes [4, 5].

[1] C. Attaccalite, M. Grüning, A. Marini, *Phys. Rev. B*, **84**, 245110 (2011)

[2] E. Perfetto, D. Sangalli, A. Marini, G. Stefanucci, *Phys. Rev. Materials*, **3**, 124601 (2019)

[3] D. Sangalli, *Phys. Rev. Materials*, **5**, 083803 (2021)

[4] H. Chen, D. Sangalli, M. Bernardi, *Phys. Rev. Lett.*, **125**, 107401 (2020)

[5] D. Sangalli, E. Perfetto, G. Stefanucci, A. Marini, *Eur. Phys. J. B*, **91**, 171 (2018)

Ab initio calculation of moiré excitons in twisted MoS₂/MoSe₂ heterostructures

Manish Jain¹, Sudipta Kundu¹, H. R. Krishnamurthy¹, Sivan Refaely-Abramson²

¹Indian Institute of Science Bangalore, India

²Weizmann Institute of Science, Israel

Abstract: Moiré heterostructures of transition metal dichalcogenide (TMD) exhibit novel optical phenomena, such as the emergence of interlayer excitons. The nature of interlayer and intralayer excitons depends on the twist angle, allowing for the tunability of their decay mechanisms and lifetimes. However, to date, most theoretical calculations of exciton properties in twisted TMD heterostructures are based on model moiré potentials. An ab-initio understanding of the excitons in these systems is crucial to not only interpret experiments, but also design heterostructures with desired properties. In this work, we study interlayer and intralayer excitons in a twisted MoS₂/MoSe₂ heterostructure using many-body perturbation theory. We present a new approach to unfold moiré excitons from the moiré

Brillouin zone to the Brillouin zones of the pristine layers composing the heterostructures. Applying this method to the twisted MoS₂/MoSe₂ heterostructure, we find that the optically forbidden momentum-indirect electron-hole transitions become allowed in the heterostructure. Our findings suggest a pathway to control and brighten dark excitons in TMDs by tuning the twist angle.

An ab-initio framework for phonon mediated exciton diffusion in crystals

Jonah Haber¹, Felipe da Jornada², Sivan Refaely-Abramson³, Diana Qiu⁴, Gabriel Antonius⁵, Steven Louie¹, Jeffrey Neaton¹

¹UC Berkeley, United States

²Stanford University, United States

³Weizmann Institute, Israel

⁴Yale University, United States

⁵University of Quebec, Canada

Developing a predictive first principles framework to accurately describe phonon mediated (or limited) exciton diffusion in complex materials remains an open challenge. In organic semiconductors - a class of promising photovoltaic materials with strong light-matter interactions and near endless chemical tunability - understanding exciton transport is further complicated by the fact that exciton bandwidths and exciton-phonon coupling strengths are similar in magnitude. In turn it is unclear *a priori* whether exciton diffusion is best described by phonon-limited Boltzmann-like or thermally activated hopping-like theories. Several computational approaches have been put forward to understand exciton dynamics in the hopping or band-like regime separately; however, to date, few approaches exist which are general enough to be applied to both regimes. In this talk, using state-of-the-art density functional perturbation theory and *ab initio* Bethe-Salpeter equation approach, we put forward a self-contained framework for computing exciton diffusion coefficients in both the band-like and hopping exciton-polaron regimes. Our reciprocal-space based, linear response method explicitly takes into account the entire crystalline environment and can seamlessly be applied to study both spin-singlet and -triplet excitations. We apply our method to a select set of acene crystals shedding additional light on microscopic origins of exciton diffusion in these classic materials.

Applying the special displacement method to understand exciton-phonon interactions in 2D materials

Sahar Sharifzadeh

Boston University, United States

We utilize first-principles theory to investigate the optoelectronic properties of a series of monolayer materials, emphasizing the role of electron-phonon interactions, a phenomenon that can dominate the properties of low dimensional systems due to their reduced screening. We utilize first-principles density functional theory (DFT) and many-body perturbation theory (MBPT) to describe excited state transitions and the special displacement method recently developed by Zacharias and Giustino to describe the role of phonons. For monolayer GeSe, a promising monochalcogenide material, our calculations predict that the optical absorption spectrum is red-shifted by ~ 0.1 eV and that the Wannier exciton wavefunction is distorted due to electron-phonon interactions, with optical phonons at ~100 cm⁻¹ coupling most strongly to the excitonic state. To better understand the role of exciton-phonon interactions in low dimensions, we study the band gap renormalization for a series of 2D materials and show that the strength of electron-phonon interactions is highly dependent on the bonding structure. Overall, this framework allows for a systematic theoretical exploration of exciton-phonon coupling.

[1] T. Huang, M. Zacharias, D. Lewis, F. Giustino, S. Sharifzadeh, *J. Phys. Chem. Lett.*, **12**, 3802 (2021)

Atomistic simulations of laser-controlled exciton transfer and stabilization in symmetric double quantum dots

Annika Bande¹, Pascal Krause¹, Jean Christophe Tremblay²

¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany

²CNRS-Université de Lorraine, France

The creation, transfer, and stabilization of localized excitations are studied in a donor-acceptor Frenkel exciton model in an atomistic treatment of reduced-size double quantum dots (QDs) of various sizes [1]. The explicit time-dependent dynamics simulations carried out by hybrid time-dependent density functional theory/configuration interaction [2] show that laser-controlled hole trapping in stacked,

coupled germanium/silicon quantum dots can be achieved by a UV/IR pump–dump pulse sequence. The first UV excitation creates an exciton localized on the topmost QD and after some coherent transfer time, an IR pulse dumps and localizes an exciton in the bottom QD. While hole trapping is observed in each excitation step, we show that the stability of the localized electron depends on its multiexcitonic character. We present how size and geometry variations of three Ge/Si nanocrystals influence transfer times and thus the efficiency of laser-driven populations of the electron–hole pair states.

[1] P. Krause, J. Tremblay, A. Bande, *J. Phys. Chem. A*, **125**, 4793 (2021)

[2] G. Hermann, V. Pohl, J. Tremblay, *J. Comput. Chem.*, **38**, 2378 (2017)

Correlated phases in TMDC heterostructures

Malte Selig, Dominik Christiansen, Manuel Katzer, Andreas Knorr
TU Berlin, Germany

Excitonic insulators represent an exotic state of matter which arise from the spontaneous formation of excitons [1] and are expected to give rise to properties such as high temperature superconductivity. The experimental realization of such states is still a challenge. In the first part of the talk, we propose heterostructures of TMDC monolayers and organic molecules as a platform to realize excitonic insulators exploiting spatially indirect interlayer excitons. We calculate for the exemplary excitonic insulating candidate WS₂-F6TCNNQ the phase diagram as function of the experimentally relevant parameters: temperature, gap energy, and dielectric environment. The distinct excitonic phases show unique signatures in far-infrared to THz spectroscopy. In the second part of the talk, we will focus on the formation of non-equilibrium steady states in monolayers of TMDCs during continuous wave excitation experiments. While cw experiments are extensively performed, the underlying exciton distributions which form upon continuous wave excitation have not been studied so far. Here, we apply a microscopic theory for the exciton dynamics [2], to investigate the interplay of intervalley Coulomb exchange coupling, exciton phonon scattering [3] and exciton recombination to the formation of non-equilibrium steady states after continuous wave pumping. We clarify, how the formation of the resulting stationary states contributes to the radiative emission of TMDC excitons. Interestingly, our calculations reveal sharp features in the degree of polarization of the emitted light as a function of excess energy originating from optical phonon transitions which dominate the exchange coupling.

[1] L. Keldysh and Y. V. Kopayev, *Soviet Physics Solid State*, *USSR6*, 2219 (1965)

[2] F. Katsch, M. Selig, A. Carmele, A. Knorr, *Phys. Status Solidi B*, **255**, 1800185 (2018)

[3] M. Selig, F. Katsch, R. Schmidt, S. Michaelis de Vasconcellos, R. Bratschitsch, E. Malic, A. Knorr, *Phys. Rev. Research*, **1**, 022007 (2019)

Designing quasi-particles of light and photo-ground states

Simone Latini
MPI Hamburg, Germany

Engineering material properties via the strong light-matter coupling that can be achieved by embedding the material in an optical cavity is an attractive avenue in material design. Here, I present first principles-based results on the formation of exciton-light hybrid states in 2D crystals embedded in a cavity and illustrate the control over their energetics and brightness. I show how the strong light-matter coupling allows for the design of a three-way exciton-phonon- photon quasiparticle which shows unique features in optical response. Finally, I introduce the concept of a photo-ground state by demonstrating that the vacuum fluctuations of light can induce a change of the collective phase from paraelectric to ferroelectric in the ground state of SrTiO₃, which has thus far only been achieved in out-of equilibrium strongly excited conditions. These findings demonstrate the potential of cavity material engineering as a new paradigm for material manipulation.

Detailed insight into exciton wavefunctions from quantum chemistry computations

Felix Plasser
Loughborough University, United Kingdom

Excitons are central to our understanding of functional materials. Computational methods are becoming ever more accurate in describing their energies and wavefunctions. However, a new bottleneck is encountered in the analysis of the computations owing not only to the quantity of data produced but also because excitonic correlation effects are particularly difficult to grasp within the standard molecular orbital (MO) picture. To overcome this problem and bridge between the MO and exciton pictures of

excited states, a detailed wavefunction analysis toolbox has been implemented within about the last decade [1–3]. Within this contribution, I will show how these tools can be used to understand exciton binding effects in conjugated polymers along with methodological challenges in their description [4]. A method for visualizing correlations between the electron and hole quasiparticles will be presented [5]. Finally, it will be shown how the same approach provides deep insight into how excitation energies are modulated by exciton binding and exchange repulsion terms [6].

[1] F. Plasser, H. Lischka, *J. Chem. Theory Comput.*, **8**, 2777 (2012)

[2] S. Bäßler, F. Plasser, M. Wormit, A. Dreuw, *Phys. Rev. A*, **90**, 052521 (2014)

[3] F. Plasser, *J. Chem. Phys.*, **152**, 084108 (2020)

[4] S. Mewes, F. Plasser, A. Dreuw, *J. Phys. Chem. Lett.*, **8**, 1205 (2017)

[5] F. Plasser, *ChemPhotoChem*, **3**, 702 (2019)

[6] P. Kimber, F. Plasser, *Phys. Chem. Chem. Phys.*, **22**, 6058 (2020)

Dynamics of coherent excitons in resonantly excited semiconductors

Enrico Perfetto

University of Roma Tor Vergata, Italy

In this talk we address the non-equilibrium properties of the exciton superfluid generated when a semiconductor is illuminated by laser pulses resonant with a bright excitonic energy. This transient state is characterized by coherent oscillations of the complex superfluid condensate that induce a subgap excitonic sideband in the time-resolved ARPES spectrum [1]. The lifetime of the exciton superfluid is also discussed by considering different effects like intervalley scattering [2], phonon-induced decoherence [3], and excited-state self-consistent screening [4,5].

[1] E. Perfetto, D. Sangalli, A. Marini, G. Stefanucci, *Phys. Rev. Materials*, **3**, 124601 (2019)

[2] E. Perfetto, G. Stefanucci, *Phys. Rev. B*, **103**, L241404 (2021)

[3] G. Stefanucci, E. Perfetto, *Phys. Rev. B*, **103**, 245103 (2021)

[4] E. Perfetto, A. Marini, G. Stefanucci, *Phys. Rev. B*, **102**, 085203 (2020)

[5] E. Perfetto, Y. Pavlyukh, G. Stefanucci, *arXiv:2109.15209*

Exciton and plasmon trapping via spatial coulomb engineering in layered materials

Malte Rösner

Radboud University, Netherlands

As a result of reduced environmental polarization, the Coulomb interactions in layered materials are in general enhanced and long-range in nature, which yields, e.g., strongly bound electron-hole pairs in semiconducting as well as pronounced plasmons in metallic monolayers. Simultaneously, modifications to the environmental screening can significantly affect the Coulomb interactions, which thus allows for an external and non-invasive control of the resulting many-body effects.

Here, I will present a combined experimental-theoretical study on how spatially varying dielectric environments can be utilized to induce sizeable band-gap modulations and significant excitonic shifts in monolayer WS₂ [1]. Based on these results I will discuss how this spatial Coulomb engineering scheme can be used to create fundamentally new heterojunctions [2] which are capable of spatially trapping excited excitons [3]. Finally, I will give an outlook on how these novel heterostructures also allow for trapping and guidance of plasmons upon optical excitations [4].

[1] L. Waldecker, A. Raja, M. Rösner, C. Steinke, A. Bostwick, R. Koch, C. Jozwiak, T. Taniguchi, K. Watanabe, E. Rotenberg, T. Wehling, T. Heinz, *Phys. Rev. Lett.*, **123**, 206403 (2019)

[2] C. Steinke, T. Wehling, M. Rösner, *Phys. Rev. B*, **102**, 115111 (2020)

[3] C. Steinke, D. Mourad, M. Rösner, M. Lorke, C. Gies, F. Jahnke, G. Czycholl, T. Wehling, *Phys. Rev. B*, **96**, 045431 (2017)

[4] Z. Jiang, S. Haas, M. Rösner, *2D Mater.*, **8**, 035037 (2021)

Exciton dynamics in atomically thin transition metal dichalcogenides

Xavier Marie

INSA Toulouse, France

In this talk I will first recall briefly the general properties of 2D excitons in Transition Metal Dichalcogenides (TMD) monolayers: giant binding energy, oscillator strength, exchange interactions, spin/valley... [1]. Encapsulation of TMD monolayers in hexagonal boron nitride (hBN) yields narrow optical transitions approaching the homogeneous exciton linewidth [2,3]. We demonstrate that the exciton radiative rate in these van der Waals heterostructures can be tailored by a simple change of the hBN encapsulation layer thickness as a consequence of the Purcell effect [4]. We also measured the exciton fine structure of MoS₂ and MoSe₂ monolayers encapsulated in boron nitride by magneto-photoluminescence spectroscopy in magnetic fields up to 30 T [5,6]. Finally I will present recent experimental results on spin/valley pumping of resident electrons in WSe₂ and WS₂ monolayers [7]. The relaxation and darkening of excitonic complexes due to efficient exciton-electron and trion-electron interactions will also be discussed [8].

- [1] G. Wang, A. Chernikov, M. Glazov, T. Heinz, X. Marie, T. Amand, B. Urbaszek, *Rev. Mod. Phys.*, **90**, 021001 (2018)
- [2] F. Cadiz, E. Courtade, C. Robert, G. Wang, Y. Shen, H. Cai, T. Taniguchi, K. Watanabe, H. Carrere, D. Lagarde, M. Manca, T. Amand, P. Renucci, S. Tongay, X. Marie, B. Urbaszek, *Phys. Rev. X*, **7**, 021026 (2017)
- [3] G. Wang, C. Robert, M. Glazov, F. Cadiz, E. Courtade, T. Amand, D. Lagarde, T. Taniguchi, K. Watanabe, B. Urbaszek, X. Marie, *Phys. Rev. Lett.*, **119**, 047401 (2017)
- [4] H. Fang, B. Han, C. Robert, M. Semina, D. Lagarde, E. Courtade, T. Taniguchi, K. Watanabe, T. Amand, B. Urbaszek, M. Glazov, X. Marie, *Phys. Rev. Lett.*, **123**, 067401 (2019)
- [5] C. Robert, H. Dery, L. Ren, D. Van Tuan, E. Courtade, M. Yang, B. Urbaszek, D. Lagarde, K. Watanabe, T. Taniguchi, T. Amand, X. Marie, *Phys. Rev. Lett.*, **126**, 067403 (2021)
- [6] C. Robert, B. Han, P. Kapuscinski, A. Delhomme, C. Faugeras, T. Amand, M. Molas, M. Bartos, K. Watanabe, T. Taniguchi, B. Urbaszek, M. Potemski, X. Marie, *Nat. Commun.*, **11**, 4037 (2020)
- [7] C. Robert, S. Park, F. Cadiz, L. Lombez, L. Ren, H. Tornatzky, A. Rowe, D. Paget, F. Sirotti, M. Yang, D. Van Tuan, T. Taniguchi, B. Urbaszek, K. Watanabe, T. Amand, H. Dery, X. Marie, *Nat. Commun.*, **12**, 5455 (2021)
- [8] M. Yang et al, *Arxiv* 2110.00887 (2021)

Exciton manipulation and transport in 2D semiconductor heterostructures

Andras Kis

EPFL, Switzerland

The discovery of graphene marked the start of research in 2D electronic materials which was expanded in new directions with MoS₂ and other layered semiconducting materials. They have a wide range of interesting fundamental properties and potential applications. New opportunities are enabled by the band structure of transition metal dichalcogenides (TMDCs) in which we could harness the valley degree of freedom for valleytronics and next-generation photonics. Long-lived interlayer excitons in van der Waals heterostructures based on TMDCs have recently emerged as a promising platform for this, allowing control over exciton diffusion length, energy and polarization. I will show here how by using MoS₂/WSe₂ van der Waals heterostructures, we can realize excitonic transistors with switching action, confinement and control over diffusion length at room temperature in a reconfigurable potential landscape. On the other hand, the weak interlayer interaction and small lattice mismatch in MoSe₂/WSe₂ heterostructures results in brightening of forbidden optical transitions, allowing us to resolve two separate interlayer transitions with opposite helicities and meV-scale linewidths. These have opposite helicities under circularly polarized excitation, either preserving or reversing the polarization of incoming light. By using externally applied electrical fields, we can control their relative intensities and polarization by different regions in the moiré pattern, characterized by different local symmetries and optical selection rules. Our more advanced excitonic devices now also offer the way to manipulate the motion of valley (spin) polarized excitons.

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Exciton optics, dynamics and transport in atomically thin materials

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Monolayer transition metal dichalcogenides (TMDs) exhibit a remarkable excitonic landscape including bright and a variety of dark exciton states. Solving 2D material Bloch equations for excitons, phonons and photons, we obtain a microscopic access to the interplay of optics, ultrafast dynamics and diffusion of excitons in TMDs. In joint theory-experiments studies we shed light on the importance of momentum-dark excitons in low-temperature photoluminescence spectra, temperature-resolved exciton-exciton annihilation, phonon-driven exciton dissociation, and accelerated hot-exciton diffusion. The gained microscopic insights into the spatiotemporal exciton dynamics are crucial for understanding and controlling many-particle phenomena governing exciton optics, dynamics and transport in technologically promising 2D materials.

Excitons and phonons in 2D perovskites

Paulina Plochocka

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High environmental stability and surprisingly high efficiency of solar cells based on 2D perovskites have renewed interest in these materials. These natural quantum wells consist of planes of metal-halide octahedra, separated by organic spacers. Remarkably the organic spacers play crucial role in optoelectronic properties of these compounds. The characteristic for ionic crystal coupling of excitonic species to lattice vibration became particularly important in case of soft perovskite lattice. The nontrivial mutual dependencies between lattice dynamics, organic spacers and electronic excitation manifest in a complex absorption and emission spectrum which detailed origin is subject of ongoing controversy. First, I will discuss electronic properties of 2D perovskites with different thicknesses of the octahedral layers and two types of organic spacer. I will demonstrate that the energy spacing of excitonic features depends on organic spacer but very weakly depends on octahedral layer thickness. This indicates the vibronic progression scenario which is confirmed by high magnetic fields studies up to 67T. Next, I will show that in 2D perovskites, the distortion imposed by the organic spacers governs the effective mass of the carriers. As a result, and unlike in any other semiconductor, the effective mass in 2D perovskites can be easily tailored. In the end, I will discuss exciton fine structure. The bright-dark splitting is also of paramount importance for light emitters which rely on the radiative recombination of excitons, since the excitons usually relax to the lowest lying dark state, which is detrimental for the device efficiency. I will discuss our optical spectroscopy measurements with an applied in-plane magnetic field to mix the bright and dark excitonic states of (PEA)₂PbI₄, providing the first direct measurement of the bright-dark splitting. The induced brightening of the dark state allows us to directly observe an enhancement of the absorption at the low-energy side of the spectrum related to the dark state. The evolution of the PL signal in the magnetic field, suggests that at low temperatures the exciton population is not fully thermalized due to the existence of a phonon bottle-neck, which occurs due to the specific nature of the exciton-phonon coupling in soft perovskite materials.

Excitons and quantum light-matter interactions in 2D materials

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Atomically thin two-dimensional (2D) materials represent a rapidly moving frontier of condensed matter physics. The reduced phase space and low dielectric screening equip these extremely thin materials with unique physical properties, which can be further tuned by external probes or by stacking the 2D materials into van der Waals heterostructures. Of particular interest are the excitonic properties of 2D semiconductors. In this talk I will discuss various features of intra-layer and (mixed) interlayer (IL) excitons in 2D semiconductors and their bilayers. These include the transition from non-Hydrogenic to Hydrogenic Rydberg series in TMD monolayers when substrate screening is increased [1] and the room temperature electrical field control of mixed IL excitons in bilayer MoS₂ [2]. I will also present our efforts in the direction of high-throughput computation of excitons in 2D materials. Finally, I will discuss how DFT can be combined with macroscopic QED to model light-matter interactions in systems that require ab initio description of the electrons, a fully nonlocal treatment of the light-matter interaction (i.e. beyond the dipole approximation), and a quantum description of both propagating and lossy light modes. The method is used to demonstrate the extremely large Purcell factors achievable by coupling a TMD quantum wells coupled to a plasmon carrying graphene sheet.

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Exploring excitonic excitations through their momentum coordinates

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Optical techniques have provided us with rich information about the exciton – a two-particle photoexcited state in semiconductors and insulators. Yet, they have left a fundamental degree of freedom of the exciton inaccessible – its *momentum*!

Over the past decade, my lab developed novel time-resolved photoemission spectroscopy techniques that have yielded valuable insights into perovskite photovoltaic materials and other semiconductor structures [1, 2, 3, 4]. In this talk, I will discuss the application of these techniques to access the momentum coordinate of excitons in 2D semiconductors, thereby providing us the formation pathways of momentum-forbidden dark excitons [5], an image of the distribution of the electron around the hole in the exciton [6], the degree of localization of the center of mass coordinate of the exciton in a moiré cell [7], and how the exciton could alter the electronic structure of the material.

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Exploring many-body effects on the dynamics of optical excitations in low-dimensional materials

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In low-dimensional and nanostructured materials, the optical response is dominated by correlated electron-hole pairs---or excitons---bound together by the Coulomb interaction. Understanding the energetics and dynamics of these excitons is essential for diverse applications across optoelectronics, quantum information and sensing, as well as energy harvesting and conversion. By now, it is well-established that these large excitonic effects in low dimensional materials are a combined consequence of quantum confinement and inhomogeneous screening. However, many challenges remain in understanding their dynamical processes, especially when it comes to correlating complex experimental signatures with underlying physical phenomena through the use of quantitatively predictive theories. In this talk, I will discuss how the dynamics of excitons in low-dimensional and nanostructured materials, such as monolayer transition metal dichalcogenides, few-layer black phosphorus, carbon nanotubes, and acene molecular crystals, differ from typical bulk materials. In particular, we will look at how symmetry and dimensionality manifest in the exciton band structure and how those features of the band structure carry over into exciton dynamics, transport, and diffusion. For instance, we find that discontinuities in the exciton dispersion introduced by the long-range exchange interaction gives rise to an unexpected nodal structure in the time-evolution of the exciton density. I will also discuss new methods we have developed to simulate exciton dynamics, including exciton-phonon interactions, and core-level excitations associated with x-ray absorption spectra.

Heralded spectroscopy of quantum confined nanoscale emitters

Dan Oron

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Multiply-excited states in semiconductor nanocrystals feature intriguing physics and play a crucial role in nanocrystal-based technologies. While photo-luminescence provides a natural probe to investigate these states, room temperature single-particle spectroscopy of their emission has so far proved elusive due to the temporal and spectral overlap with emission from the singly excited and charged states. In this work, we perform heralded spectroscopy of single quantum dots by incorporating the rapidly developing technology of single-photon avalanche diode arrays in a spectrometer setup. This allows us to directly observe the biexciton-exciton emission cascade and to measure the biexciton binding energy of single nanocrystals at room temperature, even though it is well below the scale of thermal broadening of the transitions due to finite temperature and that of spectral diffusion, the shift of the transition energy due to fluctuating electric fields. Single-particle heralded spectroscopy enables us to identify correlations of the biexciton binding energy with both charge-carrier confinement and fluctuations of the local electrostatic potential, which are masked in ensemble measurements, and to overcome artifacts due to inhomogeneous broadening. Time-resolved spectrometry, as demonstrated here, has the potential of greatly extending our understanding of charge carrier dynamics in multielectron systems and of parallelization of quantum optics protocols.

Impact of strong exciton-phonon interactions and anharmonicity on the optoelectronic properties of organic semiconductors

Antonios Alvertis

Lawrence Berkeley National Lab, United States

The molecular character of organic semiconductors often leads to strong exciton-phonon interactions, making their first-principles description challenging. In this talk, I will present a method for capturing exciton-phonon coupling to all orders, based on a combination of finite differences methods for phonons with Green's function-based methods (GW-BSE) or time-dependent density functional theory, for crystalline and isolated systems respectively. I will demonstrate that the spatial extent of an exciton controls the magnitude of its coupling to phonons, as well as the nature of the phonons (low- vs high-frequency) that dominate this interaction [1]. Moreover, I will show that for several solid-state organic semiconductors, it is only possible to accurately capture the effect of phonons on their optical properties by accounting for the strong anharmonicity of long-wavelength vibrations [2]. The presented method allows for a unified picture of exciton-phonon interactions in organic semiconductors, having several implications for the optoelectronic properties of these materials. I will exhibit its application to reveal the microscopic mechanism behind the temperature dependence of exciton energies [1], as well as to show that only through accounting for the effect of vibrations can one achieve predictive accuracy for the exciton energies of crystalline molecular systems [1], but especially for organic molecules in vacuum/solution [3]. Moreover, I will describe the localizing effect of phonons on excitons and its implications for exciton dynamics [4], and present how our physical picture can be applied to minimize non-radiative decay and to understand the mechanism behind the world's most efficient red LED [5,6].

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Interrelations of lattice vibrations and optoelectronic properties in halide perovskites

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Halide perovskites (HaPs) have attracted great scientific interest in the past years, which is in part because of their unique combination of physical properties. Of particular scientific interest is the coupling of their optoelectronic to lattice-vibrational characteristics. The reason for this is that the lattice vibrations in these materials are known to be strongly anharmonic already around room temperature, which renders models based on the harmonic approximation unsuitable. In this talk, I will present our

recent findings concerning the coupling of optoelectronic and lattice vibrational phenomena in these materials. Molecular dynamics calculations in conjunction with electronic-structure theory will be used to demonstrate that the soft, polar lattice of paradigmatic HaPs leads to a range of very interesting effects in the coupling of lattice-vibrational and optoelectronic properties.

Microscopic theory of exciton-exciton annihilation in two-dimensional semiconductors

Alexander Steinhoff

University of Bremen, Germany

Auger-like exciton-exciton annihilation (EEA) is considered the key fundamental limitation to quantum yield in devices based on excitons in two-dimensional (2D) materials. Since it is challenging to experimentally disentangle EEA from competing processes, guidance of a quantitative theory is highly desirable. The very nature of EEA requires a material-realistic description that is not available to date. In my talk, I will present a many-body theory of EEA based on first-principle band structures and Coulomb interaction matrix elements that goes beyond an effective bosonic picture [1]. The presented approach consistently takes into account all electron-hole correlations on a two-particle level. We apply our theory to quantify EEA coefficients in hBN-encapsulated monolayer MoS₂ and analyze how different Bloch states contribute to the exciton-exciton scattering. We obtain an EEA coefficient on the order of $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, suggesting that carrier losses are often dominated by other processes, such as defect-assisted scattering. We also study the influence of temperature and dielectric environmental screening on EEA, finding an inverse temperature dependence that is much stronger than the dependence on substrate dielectric constants.

Our studies open a perspective to quantify the efficiency of intrinsic EEA processes in various 2D materials in the focus of modern materials research.

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Moiré heterostructures: a condensed matter quantum simulator

Dante Kennes

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We propose twisted van der Waals heterostructures as an efficient, reliable and scalable quantum platform that enables the seamless realization and control of a plethora of interacting quantum models in a solid state framework. These new materials hold great promise to realize novel and elusive states of matter in experiment. We survey these systems as platform to study strongly correlated physics and topology that is notoriously difficult to study computationally [1]. Among the features that make these materials a versatile toolbox are (i) tunability of properties via readily accessible external parameters (such as gating, straining, packing and twist angle), (ii) ability to realize and control a large number of fundamental many-body quantum models relevant in the field of condensed matter physics and beyond and (iii) state-of-the-art experimental readouts exist to directly map out their rich phase diagrams in and out of equilibrium.

This general framework, besides unravelling new phases of matter, permits to identify their key microscopic ingredients and therefore to robustly realize and functionalize those new phases in other material systems, deepening our fundamental understanding and holding many promises for future technological applications. As examples we discuss our recent findings in twisted bilayer graphene, bilayer BN, double bilayer graphene, bilayer WSe₂, bilayer MoS₂, bilayer GeSe and generalizations to three dimensions [2].

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Narrowband high-lying excitons in transition metal dichalcogenide monolayers and bilayers

Kaiqiang Lin

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Monolayer transition-metal dichalcogenides (TMDCs) show a wealth of exciton physics. Here, we present the existence of a new excitonic species, the high-lying exciton (HX), in transition metal dichalcogenide monolayers with almost twice the band-edge A-exciton energy and with a linewidth as narrow as that of band-edge excitons (Figure 1) [1]. The HX is populated through momentum-selective optical excitation in the K-valleys, and is identified experimentally in upconverted photoluminescence (UPL) and theoretically in *ab initio* GW-BSE calculations. The coincidence of such high-lying excitonic species at around twice the energy of band-edge excitons explains the efficient exciton-exciton annihilation, and enables the excitonic quantum-interference phenomenon revealed in optical second-harmonic generation (SHG) [2]. High-lying excitons in bilayer WSe₂ can be largely tuned by twisting [3] and Stark effect, which gives control over the excitonic quantum interference and the corresponding optical nonlinearity.

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Nonradiative recombination and hot carrier cooling through conical intersections

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Non-radiative recombination limits the efficiencies of semiconductor-based optoelectronic devices and photocatalysts by converting useful electronic energy into heat. It has been known for more than half a century that such recombination is facilitated by defects, but theoretical prediction of exactly which defects promote non-radiative recombination remains a challenge. In order to develop a predictive understanding of the role specific defects play in semiconductor photophysics, we have investigated the hypothesis that conical intersections between potential energy surfaces introduced by defects form pathways for recombination. We will present recent developments in the computational identification of such defect-induced conical intersections. Fast and stable graphics processing unit accelerated multireference electronic structure codes enable the identification of these defects, and new nonadiabatic molecular dynamics methods allow us to model dynamics in their vicinities. These tools have enabled us to identify defect-induced conical intersections in silicon nanomaterials, lead-halide perovskites, and chalcogenide nanomaterials, responsible both for recombination to the electronic ground state and for cooling of excited charge carriers. Through analysis of these intersections, we can understand how the structures of these materials determine their photophysical properties.

Optical spectroscopy in the condensed phase: how to capture disorder, anharmonicity, & dynamical effects

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Exciton dynamics in solvated chromophores and molecular aggregates play a fundamental role in processes ranging from photosynthesis to vision and energy conversion in photovoltaic devices. These essential processes often depend sensitively on the interactions between a chromophore and its complex environment. Optical techniques spanning linear absorption to nonlinear and time-resolved electronic and vibrational spectroscopies provide versatile tools to investigate and ultimately control these processes. However, linking these spectroscopies to the electronic and nuclear dynamics that give rise to them in the condensed phase remains a theoretical challenge due to the need to accurately describe the ground- and excited-state electronic surfaces and combine them with methods that can capture effects arising from the thermal exploration of anharmonic nuclear motions such as torsions as well as spectral signatures of dynamical effects such as vibronic progressions. In this talk, I will show how we combine ideas in quantum dynamics and statistical mechanics with insights about separation of time and length scales to both accurately capture the linear and multidimensional electronic spectroscopy of condensed phase systems and provide a physical interpretation of the dynamical correlations and couplings between the chromophore and its environment that lead to the key features of optical spectra.

Phonon screening of excitons in lead-halide perovskite semiconductors and beyond

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First principles understanding of the electron-hole interactions in semiconductors and insulators is of fundamental importance for the development of novel light absorbers and light emitters for optoelectronic applications. The dielectric environment in which photogenerated electrons and holes interact, generally originates both from electrons and phonons. State of the art methodology for understanding single and multi-particle excitations from first principles, the GW+BSE framework, formally neglects dynamical lattice effects on the dielectric screening, and accounts only for the electronic contribution [1]. In this talk I will present our recent development of a new ab initio framework to include the contribution of dynamic phonon screening effects of electron-hole interactions into the BSE [2]. I will show that phonon screening effects can contribute to significantly reduce the exciton binding energy, partially explaining the systematic overestimation of calculated exciton binding energies with respect to experiment. I will discuss application of this new method for a range of semiconductors including leadhalide perovskites CsPbX₃ (X=Cl, Br, I), as well as semiconductors within the III-V, and II-VI series. In addition, I will rationalize results, using a generalized Wannier-Mott model which includes phonon screening from a single dispersionless polar mode, and discuss the general intuition for phonon contribution to the exciton binding energy. Finally, I will present our outlook for understanding the impact of phonons on the formation and energies of excitons. This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC), the US Department of Energy (DoE) within the C2SEPEM center, and benefited from computational resources at the National Energy Research Scientific Computing Center (NERSC) and the Texas Advanced Computing Center (TACC)

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Phonon-driven Rashba-Dresselhaus effect

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The Rashba-Dresselhaus effect is the splitting of doubly degenerate band extrema in semiconductors, accompanied by the emergence of counter-rotating spin textures and spin-momentum locking. In this talk we will discuss some recent work on the relation between lattice vibrations in solids and the Rashba-Dresselhaus effect. At an intuitive level, vibrations break inversion symmetry and therefore should lead to band splitting and spin reorientation. A natural question that emerges is under which conditions phonons and the electron-phonon interactions can induce a dynamic Rashba-Dresselhaus effect. To answer this question, we performed a detailed analysis of the energy splitting using a many-body approach. We found that, in non-magnetic crystals with an inversion center, an equilibrium phonon population does not induce band splitting to any order of perturbation theory. Conversely, a non-equilibrium phonon population can lead to sizable band splitting. In particular, we show that by coherently exciting long-wavelength infrared-active phonons it should be possible to establish spin textures with Rashba, Dresselhaus, or Weyl patterns depending on the symmetry of the vibrational eigenmodes. We discuss the experimental feasibility of this proposal by considering the photoluminescence of light-driven lead halide perovskites.

Phonon-exciton interactions in superatomic materials

Milan Delor

Columbia University, United States

I will discuss how we engineer quantum properties in two-dimensional (2D) superatomic materials, a new class of ultra-manipulable and hierarchical systems whose functional building blocks can be individually addressed to tune electronic, nuclear and spin degrees of freedom with unprecedented control. In a class of designer 2D superatomic materials, we realize unusually strong coupling between delocalized coherent phonons and electronic excitations. Leveraging this strong coupling, we achieve coherent and directional electronic transport over macroscopic lengthscales by making electrons ‘surf’ on optically-generated phonons that propagate as waves, a process we can monitor and control in real space and time using spatiotemporally-resolved microscopy.

Quantum transport of excitons in 2D semiconductors

Mikhail Glazov

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In two-dimensional transition metal dichalcogenides, tightly bound excitons dominate the optical response. It opens up a way to study transport effects optically by directly monitoring exciton propagation in space and time. The critical parameter describing the transport properties is the diffusion coefficient D . In the classical approach based on the Boltzmann equation, D is determined by the thermal velocity of excitons and mean free path. In my talk, we discuss quantum corrections to the exciton diffusion coefficient caused by the weak localization effect. We demonstrate unusual temperature dependence of the quantum correction: Its absolute value increases with increasing the temperature. We discuss experimental manifestations of nonclassical exciton diffusion. The role of exciton spin and valley degrees of freedom in the weak localization effect are analyzed. We also outline other phenomena, including the valley Hall effect, where quantum effects in exciton transport are crucial.

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Revealing electron dynamics in real time with time-dependent density functional theory

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By solving the Kohn-Sham equations in real time, time-dependent density functional theory allows for studying electron dynamics with spatial and temporal resolution and beyond the linear response regime. This talk will first shortly outline the computational approach. We then show that real-time simulations can directly reveal the many body character of electronic excitations. Our example refers to an organic semiconductor that is first excited by one light pulse, and then ionized by a second light pulse. The angular resolved photoemission signal (ARPES) that results after the second pulse can be interpreted as an (approximate) visualization of the momentum distribution of the excited state. We show that one can directly see the many-particle character of the excitation in the ARPES signal, and that thinking about the process in the one-particle picture of “an electron moving from one orbital to another orbital” can be misleading. We also address the question of the accuracy of the employed exchange-correlation approximation, and we discuss recent developments of using meta-Generalized Gradient Approximations in time-dependent calculations.

Simulating exciton transport in molecular aggregates with quantum-classical mapping methods

Aaron Kelly

Max Planck Institute for the Structure and Dynamics of Matter, Germany

We discuss aspects related to simulating exciton transport in molecular aggregates in real-time, and at finite temperature. In particular, we show how the exciton mobility can be obtained by employing highly efficient, and reasonably accurate, quantum-classical mapping methods. The temperature dependence of the exciton mobility is also discussed with a focus on Frenkel-Holstein-type models that have been adapted to represent molecular aggregates in one-, two-, and three-dimensions.

Simulating THz field-induced ferroelectricity in quantum paraelectric SrTiO₃

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By applying the light on materials, various intriguing properties are observed against their ambient condition. For example, it is experimentally demonstrated that light can enhance the critical temperature for superconductivity in K₃C₆₀. Recent studies revealed that ferroelectricity can be achieved by applying light on the quantum paraelectric SrTiO₃ [1-2]. Here, we investigate the microscopic mechanism of terahertz (THz) field-induced ferroelectricity in quantum paraelectric SrTiO₃. We first investigate the description of quantum paraelectric phase in SrTiO₃ [3]. Based on the density functional theory calculations, we find that the quantum description between ferroelectric soft mode and lattice strain is required to evaluate the properties of the quantum paraelectric SrTiO₃. With this understanding, we investigate THz field-induced ferroelectricity by solving Schrodinger-Langevin equation [4]. Our calculation results indicate that the microscopic mechanism of this phenomenon is light-mixed state between ground and the first excited states of ferroelectric soft mode in the quantum paraelectric phase. Our studies provide microscopic understanding of the quantum paraelectric and related THz field-induced phenomenon.

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Spatial and temporal imaging of exciton transport in two-dimensional heterostructures

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Charge-transfer (CT) excitons at hetero-interfaces play a critical role in light to electricity conversion using nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. Atomically thin and two-dimensional (2D) nanostructures provide a new platform to create architectures with sharp interfaces for directing interfacial exciton transport. Here we investigate the formation and transport of interlayer CT excitons in van der Waals (vdW) heterostructures based on semiconducting transition metal dichalcogenides (TMDCs) employing transient absorption microscopy (TAM) with a temporal resolution of 200 fs and spatial precision better than 50 nm.

We have investigated interlayer exciton dynamics and transport modulated by the moiré potentials in WS₂-WSe₂ heterobilayers in time, space, and momentum domains using transient absorption microscopy combined with first-principles calculations. Experimental results verified the theoretical prediction of energetically favorable K-Q interlayer excitons and unraveled exciton-population dynamics that was controlled by the twist-angle-dependent energy difference between the K-Q and K-K excitons. Spatially- and temporally-resolved exciton-population imaging directly visualizes exciton localization by twist-angle-dependent moiré potentials of ~100 meV. Exciton transport deviates significantly from normal diffusion due to the interplay between the moiré potentials and strong many-body interactions, leading to exciton-density- and twist-angle-dependent diffusion length. These results have important implications for designing vdW heterostructures for exciton and spin transport as well as for quantum communication applications.

Spectroscopy and charge sensing using defects in van der Waals layers

Hadar Steinberg

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In recent years, we experience a surge of interest in the role of defects in exfoliated system as quantum probes. Assembly of layers which carry atomic sized defects can facilitate the tunability and the use of such defect-based probes at very close proximity to systems which we are interested in probing. In my talk, I will describe our group's work on tunnel junctions, fabricated by placing a thin insulator on top of a layered material [1]. I will then show how defects, often present in the tunnel barrier, function as atomic-sized quantum dots. When strongly coupled to a superconductor, these dots give rise to Andreev bound states [2]. When weakly coupled, the dots exhibit sharply resolved resonant tunneling conductance features, strongly dependent on the energy of the dot state. When a graphene electrode is used, electric field applied by an external gate penetrates the graphene layer, tuning the dot energy. The result is an energy-tunable dot, deployed at atomic distance from a system of choice. I will discuss several applications of such dot-assisted measurements, including use of dots as sensitive spectrometers of superconductors [3], or as single electron transistors, which reveal unusual features in the density of states of the graphene layer at high magnetic fields [4].

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Strong interactions in correlated dipolar quantum fluids of excitons and polaritons

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Quantum fluids of matter with long range, anisotropic interactions display rich emergent collective phenomena, from Roton instabilities, quantum droplets, and supersolidity [1]. A prominent example is the dipole-dipole interaction, which has recently been addressed by a growing community, both from atomic physics as well as from condensed matter physics, with the latter being focused on dipolar quantum fluids of two-dimensional excitons, and very recently, on the introduction of interacting dipolar polaritons. These strongly interacting dipolar exciton and polariton systems offer opportunities to explore new collective phenomena which are currently inaccessible with atomic dipolar gases, and the possibility to demonstrate new types of quantum devices on the level of two-particle interaction. We will present several recent results in systems of dipolar excitons and polaritons. These include strong experimental evidence for the dynamical formation of a robust dark dense liquid phase of dipolar excitons in a bilayer system, and a dynamical transition to a gray condensate [2]. The experiments are corroborated by a theory explaining the remarkable stabilization of a dense dark-spin exciton Bose-Einstein condensate as driven by particle dipolar interaction induced correlations. Also, I will report on the observation of a formation of an attractive di-polaron-like many-body correlated state [3]. This effect, which is due to the anisotropic nature of the dipole-dipole interaction, takes place in a new structure design allowing vertical coupling of dipolar exciton fluids, and is a first step towards realizing an exciton supersolid, recently observed in atomic dipolar systems [1]. Finally, I will introduce recent experiments showing formation of flying electrically polarized dipolar-polaritons ('dipolaritons') in optical waveguides, resulting in a large, electrically tunable enhancement of the polariton-polariton interactions [4], a result promising for future implementations of a dipolar polariton blockade and quantum circuitry.

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Theory of excitons in 2D magnet materials - interlayer interactions and entanglement

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The research on atomically thin 2D materials has opened opportunities in exploring new material properties and related applications absent in conventional bulk materials. In this talk, we will present our recent theoretical and first-principles studies of excitons in 2D magnetic semiconductors. We show that 2D magnetic semiconductors exhibit a rich set of excitons of Frenkel or Wannier types, which encode excited-state information dictated by the underlying crystal structure and magnetic order. We then present our recent study of the roles of interlayer couplings on the excitons and optical properties of these materials. By first-principle calculations based on many-body perturbation theories, we find that the interlayer couplings and entanglement of excitons can be tuned by external fields. We further connect our theoretical discoveries to experimental results and explore their potential applications.

Theory of the exciton-phonon coupling

Gabriel Antonius

University of Quebec, Canada

The effects of the electron-phonon interaction on optical excitations can be understood in terms of exciton-phonon coupling, and require a careful treatment in low-dimensional materials with strongly bound excitons or strong electron-hole interaction in general. Through phonon absorption and emission processes, the optically accessible excitons are scattered into otherwise optically dark finite-momentum exciton states. We derive a practical expression for the phonon-induced term of the exciton self-energy (denoted as the exciton-phonon self-energy) that gives the temperature dependence of the optical transition energies and their lifetime broadening resulting from the exciton's interaction with the phonons. We illustrate this theory on a two-dimensional model, and show that our expression for the exciton-phonon self-energy differs qualitatively from previous expressions found in the literature that neglect the exciton binding or electron-hole correlations

Towards mixed quantum-classical simulations of nonequilibrium phenomena in bulk and low-dimensional materials

Roel Tempelaar

Northwestern University, United States

The recent years have seen an increased interest in crystalline materials that feature strong coupling of electronic carriers to lattice vibrations, examples of which include bulk and low-dimensional perovskites as well as monolayer transition-metal dichalcogenides. Strong electron-vibrational coupling has been well studied in molecular assemblies, where mixed quantum-classical (MQC) dynamics has emerged as one of the most potent simulation tools. MQC dynamics takes the classical approximation for the vibrational modes, while being otherwise nonperturbative and capable of describing strong couplings at high accuracy and at low computational cost. The involved equations of motion are traditionally solved in real space. This is appropriate for most molecular assemblies, as the involved excitations tend to localize and are well described by restricting the quantum and classical bases to the local regions of interest. For crystalline materials with band-like properties, however, excitations are delocalized over exceedingly large spatial domains. In this talk, I will present our recent efforts aimed at reformulating MQC dynamics within a reciprocal-space representation tailored to describing fully-delocalized, Bloch-like excitations. Since such excitations tend to "localize" in select regions of the Brillouin zone, computations can be kept feasible by truncating the transformed electronic and vibrational bases to the regions of interest. Proof-of-principles results will be presented for both mean-field (Ehrenfest) MQC dynamics and for fewest-switches surface hopping. The latter is shown to yield accurate short- and long-time behavior when compared against numerically-exact results, offering exciting prospects for the simulation of nonequilibrium phenomena in bulk and low-dimensional materials.

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Tracking exciton dynamics in time and space with sub-10fs time-resolution and sub-10nm spatial precision

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Key to understanding exciton dynamics in nanoscale materials is the experimental capability to track the dynamics of excitons on their native time and length scales. In this talk I will describe recent results emerging for our fs-transient absorption microscopy methodology that allows us to track exciton dynamics in a range of materials with sub-10fs time-resolution and sub-10nm spatial precision. This allows us for the first time to watch exciton dynamics before decoherence kicks in and correlate with underlying sample morphology. This allows us to provide new insights into exciton transport in molecular materials via 'transient delocalization' [1], coherent light-matter coupling with cavity free polaritons [2] and the dynamics of room-temperature exciton condensates [3].

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Ultrafast transfer processes and exciton-exciton interactions in (functionalized) atomically thin semiconductors

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Atomically thin semiconductors constitute a remarkable playground for exciton physics in two dimensions. This involves optically accessible (bright) as well as spin- and momentum-forbidden (dark) excitonic states including intravalley and intervalley excitations [1]. The nonlinear, coherent exciton dynamics induced by short light pulses results from the interplay of intrinsic exciton-exciton [2] and exciton-phonon [3] interactions. Here, we present applications of the theory to:

- biexcitons and exciton-exciton scattering induced coherence decay [4],
- detection of exciton wave function dynamics in time resolved ARPES [5,6], and
- different charge-, Dexter- or Förster-type transfer processes in atomically thin semiconductors functionalized with organic molecules or graphene [7].

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- [2] F. Katsch, et al., *Phys. Stat. Sol. (b)* **255**, 1800185 (2018)
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Γ -to- Γ optical transitions in van der Waals heterostructures of 2D materials

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We propose to use 2D materials to produce type-II heterostructures with Γ -point band edges for applications in optoelectronics. The family of such materials includes atomically thin films of n-type InSe, GaSe [1] and few-layer films of p-type transition metal dichalcogenides (WSe₂, WS₂, MoSe₂, MoS₂) [2]. We show that such heterostructures offer efficient interlayer coupling, promoting layer-indirect optical transitions, which cover a broad range of the visible spectrum, depending on the composition of the heterostructures [3]. Also, the layer-indirect excitons in such systems have the out-of-plane electric dipole moments which are larger than in bilayer heterostructures of 2D materials, which enhances their repulsion and offers stronger sensitivity of the PL response to the exciton density, including a higher temperature for the exciton condensation. A broader family of Γ - Γ interfaces may include hybrids of InSe, GaSe and few-layer TMDs with phosphorene, where the spectral range of transition extends into the IR range. Also, we show that few-layer films of such materials feature optically active inter-subband

transition that cover densely the IR-THz range [4], which can be excited by the carrier injection in vertical tunnelling devices [5]. We also note that photons emitted in the proposed systems are generated by the electric dipole transition and have an out-of-plane linear polarization, which would require a specific electromagnetic environment for their efficient implementation in optoelectronics devices, different from the cavity resonators used for monolayer TMD crystals.

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4. Posters

A novel quantum-classical approach to exciton dynamics in condensed phase systems

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Nonlinear spectroscopy offers a powerful tool for investigating microscopic quantum dynamics. In particular, such techniques have been the experimental method of choice for investigating the excitonic energy-transfer processes within photosynthetic light-harvesting systems, where researchers have speculated that inherent quantum effects are necessary to explain their amazing ability to harvest sunlight with near perfect quantum efficiency [1]. However such spectroscopic quantities are often challenging to obtain theoretically for complex condensed phase systems, due to the large number of degrees of freedom. Semiclassical approximations for the full exciton-nuclear dynamics can be derived with the use of mapping variables [2, 3]. Within these approaches the excitonic subsystem is mapped exactly onto a fictitious system, which has a well-defined classical limit. The dynamics associated with the mapped system is then described by an ensemble of classical trajectories. In particular, we have recently developed a new mapping-based approach, called spin-mapping, which has been shown to be extremely accurate at computing dynamical quantities of interest for nonadiabatic condensed phase systems [4, 5]. In this poster, we will show how spin-mapping can be applied to accurately and efficiently compute the various optical response functions that contribute to the nonlinear optical spectra of nonadiabatic condensed phase systems, such as a Frenkel biexciton model and the Fenna-Matthews-Olsen complex [6]. Because each optical response function is calculated independently within our approach, contributions from different dynamical pathways can be separated from the full signal, giving further insight beyond what can be achieved directly from experiment.

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Assessment of the performance of density functionals for the description of excited states of pi-conjugated TADF blue emitters

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Computational modeling of the optical characteristics of organic molecules with potential for thermally activated delayed fluorescence (TADF) [1] employs mostly the TD-DFT approach. Efficient TADF requires the development of emitters with nearly degenerate first excited singlet and triplet state. In order to obtain accurate predictions, the choice of a proper functional is crucial [2]. In the current study, we focus on testing the performance of a set of DFT functionals for estimation of the excitation and emission energy and the excited singlet-triplet energy gap of three newly synthesized compounds with capacity for TADF. The emitters are designed specifically to enable charge transfer via pi-electron conjugation, at the same time possessing high-energy excited triplet states [3]. The functionals chosen for testing are from various groups ranging from gradient-corrected through global hybrids to range-separated ones. The results show that the monitored optical properties are especially sensitive to how the long-range part of the exchange energy is treated within the functional. The accurate functional should also be able to provide well balanced distribution of the p-electrons among the molecular fragments. Global hybrids with moderate (less than 0.4) share of exact exchange (B3LYP, PBE0) and the meta-GGA HSE06 are outlined as the best performing methods for the systems under study. They are able to predict all important optical parameters correctly, both qualitatively and quantitatively.

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Between exciton dispersion and structure of carbon nanotubes from ab initio

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²Yale University, United States

Single-walled carbon nanotubes (SWCNTs) are easily tunable nanostructures that could be building blocks for different functional materials. Isolated nanotubes are known for their ability to form delocalized excitons with large binding energies. In this work, we use recent GW-BSE development to calculate excitonic band structures for the quasi 1D-systems SWCNTs. We study the relation between exciton dispersion and radiative lifetime for three different SWCNTs with different tube structures, chirality, and symmetry.

DFT calculation of electronic structure variations during doping of semiconductor materials

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In the present investigation, as a case study, the electronic structure of rutile Titanate is thoroughly investigated before and after introduction of Molybdenum dopant into the structure using density functional theory (DFT) method. The aim of this investigation is to study the variation of electronic structure of semiconductor materials by introduction of dopant into the structure which has an undeniable influence on the exciton dynamics when making heterojunctions especially in photocatalyst materials. According to calculated results, rutile has an indirect band gap, which means there is a momentum transfer during excitation and release. The lowest level of conduction band belongs to Ti 3d states, and the highest level of valance band to O 2p states. Mo doping does not have any influence on the valence band. Contradictorily, it lowers the conduction band edge (0.6 eV) by the introduction of Mo 4d states and mixing with the Ti 3d states. By introduction of Mo into the rutile structure, band gap energy value of rutile was reduced from 2.95 down to 2.35 eV. The creation of energy states below the conduction band because of Mo doping was identified as the reason for reducing the band gap energy of rutile. A meaningful change in the percentage of orbitals' engagement during excitation was also observed. As a conclusion, changing the band structure, creation of energy levels in band gap, and changing the percentage of orbitals' engagement after doping are the three important parameters influencing exciton dynamics of semiconductor materials.

Engineering excitonic effects in two-dimensional materials using advanced computational methods

Vijay Singh, Hyowon Park

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Two-dimensional materials offer various technological opportunities for future device applications and energy materials. For these applications, one needs to understand the excited properties of these materials under external perturbations such as light absorption. Excitons are the bound state of excited electrons and holes, which are frequently studied in semiconductors. However, the study of excitonic properties in new two-dimensional materials has been challenging due to the complex nature of their spin, charge, orbital, and lattice degrees of freedom. To study the strongly correlated nature of excitonic properties in these materials, we have employed advanced computational methods including density functional theory, dynamical mean field theory, and machine learning. In this presentation, we will show the many-body excitonic spectra and the strong binding energies of newly synthesized two-dimensional materials and compare them to known experimental data. Our results will advance the understanding of many-body features of excitonic properties in two-dimensional materials based on first principles

Exciton dynamics in pentacene crystal from GW-BSE

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Exciton dynamics underlie functionality for applications in optoelectronic and photophysics. Understanding the relation between time-resolved exciton evolution and material structure can lead to desirable tunability and optimal efficiency through atomistic design. In this research, we study exciton decay and diffusion processes in organic molecular crystals as a function of crystal structure. We focus on the pentacene crystal, a well-studied system with long exciton lifetimes that depend on crystal packing. By applying a first-principles approach, based on many-body perturbation theory within the GW-BSE approximation, we calculate the exciton dispersion and study its origins. We connect the exciton bandstructure to radiative and non-radiative relaxation processes. We compute an exciton wavepacket propagation in the ballistic regime and explore its relation to a longitudinal-transverse excitation energy split, stemming from the intermolecular interaction nature. We further compute band-to-band transitions and thermalization effects via a recently-developed ab initio approach to exciton-phonon interactions. Our study paves the way to predictive computations of exciton decay mechanisms and diffusion lifetimes, allowing a direct relation to the underlying crystal structure through bandstructure properties.

Exciton g-factors of van der Waals heterostructures from first principles calculations

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External fields are a powerful tool to probe optical excitations in materials. The linear energy shift of an excitation in a magnetic field is quantified by its effective g-factor. Here we show how exciton g-factors and their sign can be determined by converged first principles calculations. We apply the method to monolayer (1L) excitons in semiconducting transition metal dichalcogenides (TMDs) and to interlayer excitons in MoSe₂/WSe₂ hetero-bilayers and obtain excellent agreement with recent experimental data. The precision of our method allows to assign measured g-factors of optical peaks to specific transitions in the band structure and also to specific regions of the samples. This revealed the nature of various, previously measured interlayer exciton peaks. We further show that, due to specific optical selection rules, g-factors in van der Waals heterostructures are strongly spin and stacking-dependent. The presented approach can potentially be applied to a wide variety of semiconductors [1].

The method was successfully applied to bigger excitonic complexes: trions, their phonon replicas and biexcitons in 1L WS₂. It also overcomes the currently used simple models, yielding g-factors of individual electrons and holes in perfect agreement with their experimental values [2].

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Gate-switchable arrays of quantum light emitters in contacted monolayer MoS₂ van der Waals heterodevices

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Controlling single-photon emission on a few nanometers plays an important role for the scalability of future quantum photonic circuits. Moreover, it is highly relevant to facilitate a gate-switchable emission for quantum information schemes. By irradiating MoS₂ with helium ions, we generate single-photon sources at ~1.75 eV with a lateral position accuracy of only a few nanometers [1], which can be understood in terms of sulfur vacancies [2]. Second-order correlation measurements unambiguously

proof the nature of single-photon emission. Charge doping of the monolayer MoS₂ can be used for switching the quantum emission on and off [3]. This deterministic control of light emission in spatial and temporal means paves the way for new integrated quantum photonic technologies.

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Optical dipole orientation of interlayer excitons in MoSe₂-WSe₂ heterostacks

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Transition metal dichalcogenide monolayers exhibit strong light-matter interactions, which promotes them as ideal candidates for novel 2D optoelectronic applications. A vertical stacking into van der Waals heterostacks leads to the formation of long-lived interlayer excitons in adjacent layers. Here, we present the far-field photoluminescence intensity distribution of interlayer excitons in MoSe₂-WSe₂ heterostacks as measured by back focal plane imaging in the temperature range between 1.7K and 20K. An analytical model describing the emission pattern from a dielectric heterostructure is used to obtain the relative contributions of the in- and out-of-plane transition dipole moments associated to the interlayer exciton photon emission. We determine the transition dipole moments for all observed interlayer exciton transitions to be (99±1)% in-plane for R- and H-type stacking, independent of the excitation power and therefore the density of the exciton ensemble in the experimentally examined range [1]. Moreover, we demonstrate signatures for many-body states in the dense ensembles of interlayer excitons [2].

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TD-DFT modelling of the emission transitions of organic TADF blue light emitters

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In the past decades, there has been an enormous progress in the development of new and more efficient light sources. One of them are organic light-emitting diodes (OLEDs), which have been investigated extensively for the past 30 years [1]. Some of the modern OLEDs rely on fluorescent or phosphorescent emitters. Nowadays, there is great interest for devices that operate on the principle of thermally activated delayed fluorescence (TADF) [2]. This process employs transition from triplet to singlet excited state, which increases the efficiency of the diode. One of the most serious challenges industry faces is the development of such blue light emitters. It can be aided by molecular modeling.

The present study summarizes the results of (TD)DFT modelling aimed at designing new compounds that are suitable for blue light emission enhanced by TADF. The geometries of the molecules are optimized with B3LYP/6-31G*. Absorption and emission transitions are obtained with the TDDFT approach. Based on the results, the possibility of TADF in different molecules and their capacity to emit blue light are evaluated. The effect of combining different molecular fragments and varying substitution

positions is assessed. The most promising structures are proposed for synthesis and experimental characterization.

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The competition between photothermal effect and emission in potential phototherapy agents

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Planar donor-acceptor-donor (D-A-D) organic molecules have been highlighted as promising photothermal agents due to their good light-to-heat conversion ratio, easy degradation and chemical tunability. Very recently, it has been demonstrated that their photothermal conversion can be boosted by appending rather long alkyl chains. Despite this behavior has been tentatively associated to the population of a non-radiative twisted intramolecular charge transfer (TICT) state driven by intramolecular motion, the precise mechanisms and the role played by the environment, and most notably aggregation, still remain elusive. In this context, we carried a series of Time-Dependent Density Functional Theory (TD-DFT) calculations combined with Molecular Dynamics (MD) simulations to achieve a realistic description of the isolated and aggregated systems. Our theoretical models unambiguously evidence that the population of CT states is very unlikely in both cases, whereas the light-triggered heat dissipation can be ascribed to the activation of specific vibrational degrees of freedom related to the relative motion of the peripheral chains. Overall, our results clearly corroborate the active role played by the alkyl substituents in the photothermal conversion through vibrational motion, while breaking with the conventional picture, which invokes the formation of dark TICT states in non-close packed aggregates.

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