CECAM – Workshop

Computational insight into photo-induced processes at interfaces

October 10th – 14th 2016

Bremen Center for Computational Materials Science

University of Bremen

Program of the International CECAM-Workshop
Computational insight into photo-induced processes at interfaes

Bremen Center for Computational Materials Science – BCCMS
University of Bremen, October 10th - 14th 2016
Conference site: House of Science, Downtown

Monday, October 10th 2016 (RAMADA Ueberseehotel Bremen)

18:00 – 21:00	**Registration**

Tuesday, October 11th 2016 (House of Science Bremen, Downtown)

08:00 – 08:50	**Registration**
08:50 – 09:00	**Opening and welcome, Thomas Frauenheim**
Session:	**Photo-catalysis I**
	Chair: Oleg V. Prezhdo
09:00 – 09:40	Victor S. Batista, Yale University, New Haven, Connecticut, US *Linker rectifiers for covalent attachment of catalysts to semiconductor surfaces*
09:40 – 10:20	Harald Oberhofer, Technical University of Munich, Germany *Photo-electro-chemistry modelling beyond the computational hydrogen electrode*
10:20 – 11:00	Nikos Doltsinis, University of Muenster, Germany *Multiscale simulations of organic bulk heterojunction photovoltaics*
11:00 – 11:30	**Coffee Break**
11:30 – 12:10	Alexander L. Shluger, University College London, UK *Mechanisms of photo-induced processes at metal/insulator interfaces*
12:10 – 12:50	Zhipan Liu, Fudan University, Shanghai, China *Hetero-phase structure and its role in photocatalysis*
12:50	**Group photo**
13:00 – 14:30	**Lunch Break (Restaurant Stadtwirt) and Coffee**
Session:	**Photovoltaics I**
	Chair: Nikos Doltsinis
14:30 – 15:10	Shen Meng, Chinese Academy of Sciences, Beijing, China *Excited state dynamics in condensed matter using real time TDDFT*
15:10 – 15:50	Cristián G. Sánchez, National University of Córdoba, Argentina *A time dependent picture of ultra-fast photo-induced charge transfer, insight from models and simulations*
15:50 – 16:20	**Coffee Break**
16:20 – 17:00	Elisa Molinari, University of Modena and Reggio Emilia, Italy *Understanding the early stages of exciton formation and charge separation in organics*
19:00 – 21:30	**Welcome Reception (Bremen Town Hall)**

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Wednesday, October 12th 2016 (House of Science Bremen, Downtown)

Session:	**Devices**
	Chair: Adriel Domínguez-García
09:00 – 09:40	Chiyung Yam, Beijing Computational Science Research Center, China *Quantum mechanical modeling of nanoscale light emitting diodes*
09:40 – 10:20	Kristian S. Thygesen, Technical University of Denmark, Kgs. Lyngby *Electronic excitations and photo-induced processes in van der Waals heterostructures*
10:20 – 11:00	Thomas A. Niehaus, Claude Bernard University Lyon 1, Villeurbanne, France *Nitrogen(II) oxide charge transfer complexes on TiO_2: a new source for visible-light activity*
11:00 – 11:30	**Coffee Break**
Session:	**Light-induced excitations**
	Chair: Thomas Brumme
11:30 – 12:10	Johannes Lischner, Imperial College London, UK *Electronic excitations at solid-liquid interfaces combining GW with joint DFT*
12:10 – 12:50	David A. Strubbe, University of California, Merced, US *Solar thermal fuels: photoisomerization dynamics from TDDFT and efficiency limits for solar energy storage*
12:50 – 14:30	**Lunch Break (Restaurant Stadtwirt) and Coffee**
Session:	**Photocatalysis II**
	Chair: Kristian S. Thygesen
14:30 – 15:10	Timo Jacob, Ulm University, Germany *Modeling of electrochemical interfaces and processes*
15:10 – 15:50	Nicholas M. Harrison, Imperial College London, UK *The structure of titania surfaces and of initial water adsorption*
15:50 – 16:20	**Coffee Break**
16:20 – 17:00	Peter Deák, University of Bremen, Germany *Water splitting and the band edges positions of TiO_2*
18:40	**Bus Pickup to Conference Dinner** *(Venue: RAMADA Ueberseehotel Bremen, Wachtstraße 27-29)*
19:00 – 22:30	**Conference Dinner (Restaurant Juergenshof)**

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Thursday, October 13th 2016 (House of Science Bremen, Downtown)

Session:	**Photovoltaics II**
	Chair: Sheng Meng
09:00 – 09:40	Jeffrey B. Neaton, University of California, Berkeley, US *Excited states of organic solids and interfaces with ab initio many-body perturbation theory*
09:40 – 10:20	Sergei Tretiak, Los Alamos National Laboratory, New Mexico, US *On the way toward efficient perovskite photovoltaics and beyond*
10:20 – 11:00	Veaceslav Coropceanu, Georgia Institute of Technology, Atlanta, US *Impact of static and dynamic disorder on charge recombination in organic solar cells*
11:00 – 11:30	**Coffee Break**
11:30 – 12:10	Zhigang Shuai, Tsinghua University, Beijing, China *QM/MM studies of excited state non-radiative decay and charge mobility in molecular aggregates*
12:10 – 12:50	David Beljonne, University of Mons, Belgium *Electronic processes at organic-(in)organic interfaces*
12:50 – 14:30	**Lunch Break (Restaurant Stadtwirt) and Coffee**
Session:	**Methods**
	Chair: Tim O. Wehling
14:30 – 15:10	Steven G. Louie, University of California, Berkeley, US *Excited state phenomena and photo-physics of atomically thin 2D materials*
15:10 – 15:50	Oleg V. Prezhdo, University of Southern California, Los Angeles, US *Non-adiabatic dynamics of charge and energy transfer at nanoscale interfaces*
17:55	**Poster Mounting**
18:00 – 21:00	**Poster Session, Catering Buffet (House of Science)**

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Friday, October 14th 2016 (House of Science Bremen, Downtown)

Session:	**Time dependent processes**
	Chair: Johannes Lischner
09:00 – 09:40	Heiko Appel, Fritz Haber Institute of the Max Planck Society, Berlin, Germany *Light-matter coupling in density-functional theory for quantum electrodynamics*
09:40 – 10:20	Gang Lu, California State University, Northridge, US *Exciton dynamics in organic and perovskite photovoltaics – a large-scale TDDFT study*
10:20 – 11:00	Karsten Reuter, Technical University of Munich, Germany *Affordable first-principles modeling of charge transport: where did my holes go?*
11:00 – 11:30	**Coffee Break**
11:30 – 12:10	Adriel Domínguez-García, Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany *Excitonic quasiparticles in TiO_2*
12:10 – 12:20	***Closing words: Thomas Frauenheim***
12:30	**Departure**

Abstracts of Lectures

Linker rectifiers for covalent attachment of catalysts to semiconductor surfaces

Wendu Ding.(1,2) Matthieu Koepf (2), Christopher Koenigsmann (2), Arunabh Batra (3), Latha Venkataraman(3), Christian F. A. Negre (1,2), Gary W. Brudvig (1,2), Robert H. Crabtree.(1,2), Charles A. Schmuttenmaer (1,2) and Victor S. Batista (1,2)

(1) Yale University, Department of Chemistry, New Haven, Connecticut, United States
(2) Yale University, Energy Sciences Institute, West Haven, Connecticut, United States
(3) Columbia University, Department of Applied Physics and Applied Mathematics, New York, NY, United States

Linkers that favor rectification of interfacial electron transfer are likely to be required for efficient photo-driven catalysis of multi-electron reactions at electrode surfaces. Design principles are discussed, together with the synthesis and characterization of a specific pair of molecular frameworks, related by inversion of the direction of an amide bond at the heart of the molecule. The linkers have a terpyridyl group that can covalently bind Mn as in a well-known water oxidation catalyst and an acetylacetonate group that allows attachment to TiO2 surfaces. The appropriate choice of the sense of the amide linkage yields directionality of interfacial electron transfer, essential to enhance electron injection and slow back-electron transfer. Support comes from electron paramagnetic resonance, terahertz spectroscopic, computational modeling characterizing the asymmetry of electron transfer properties, and conductance measurements based on the scanning tunneling microscope break-junction (STM-BJ) technique.

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[4] J. Chem. Theory Comput 11: 5888–5896 (2015). Computational Design of Intrinsic Molecular Rectifiers based on Asymmetric Functionalization of N-phenylbenzamide, Wendu Ding, Matthiew Koepf, Christopher Koenigsmann, Arunabh Batra, Latha Venkataraman, Christian Negre, Gary W. Brudvig, Robert H. Crabree, Charles A. Schmuttemnaer and Victor S. Batista.

[5] New J. Chem. xxx: xxxx-xxxx (2016) Structure–function relationships in single molecule rectification by N-phenylbenzamide derivatives, Christopher Koenigsmann, Wendu Ding, Matthieu Koepf, Arunbah Batra, Latha Venkataraman, Christian F.A. Negre, Gary W. Brudvig, Robert H. Crabtree, Victor S. Batista, Charles A. Schmuttenmaer.

[6] Phys. Chem. Chem. Phys. 18: 18678-18682 (2016) Molecular design of light-harvesting photosensitizers: effect of varied linker conjugation on interfacial electron transfer, Jianbing Jiang, John R. Swierk, Svante Hedstrom, Adam J. Matula, Robert H. Crabtree, Victor S. Batista, Charles A. Schmuttenmaer and Gary W. Brudvig.

Photo-electro-chemistry modelling beyond the computational hydrogen electrode

Harald Oberhofer

Technical University Munich, Department of Chemistry,
Chair for Theoretical Chemistry, Munich, Germany

The role computer modelling plays today in understanding and optimising catalysts for photo-electrochemical reactions is undisputed. Yet, state of the art simulation approaches tend to rely on a number of assumptions and simplifications which—according to newest results—may not be fully justified. For example, simulation of the all-important electro-catalytic water oxidation reaction is mainly based on idealised surfaces and the computational hydrogen electrode (CHE) approach, which evaluates the thermodynamic feasibility of a catalyst looking at pathway where each hydrogen abstraction is coupled to the removal of one electron (PCET). This in turn is used to justify neglecting interfacial solvation effects as only overall neutral reaction intermediates need to be considered. Yet, especially on semi-conducting catalysts the assumption of PCET is not necessarily fulfilled.

The great success of the CHE approach is in part due to its low computational cost allowing a computational screening of suitable catalyst materials. Any other scheme going beyond PCET and ideal surfaces should therefore match this advantage, ideally avoiding costly molecular dynamics sampling of solvent degrees of freedom. Yet, recent developments in thermodynamic modelling as well as embedding techniques, both liquid and solid-state, especially considering the interface between catalyst and solvent, point the way towards photo-electrochemistry modelling beyond the computational hydrogen electrode.

Multiscale simulations of organic bulk heterojunction photovoltaics

Nikos Doltsinis

University of Muenster, Institute for Solid State Theory, Muenster, Germany

The morphology and electronic properties of non-fullerene organic bulk heterojunction solar cell materials is investigated using a multiscale simulation approach. First, atomistic force fields are derived from density functional theory (DFT) calculations for novel donor and acceptor components. The atomistic representation then serves as a reference for the parametrization of a coarse grained force field, which is employed to simulate the morphology of the material. Electronic properties of the material are subsequently studied by first mapping the system back onto an atomistic representation before applying first principles methods for electronic excitation energies, exciton diffusion, and charge transport.

References:

[1] M. Böckmann, N.L. Doltsinis, Can excited electronic states of macromolecules with extended pi-systems be reliably predicted? A Case Study on P3HT, Front Mater. 2 (2015) 25.

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Mechanisms of photo-induced processes at metal/ insulator interfaces

Matthew T. E. Halliday (1), Wayne P. Hess (2), Alexander L. Shluger (1)

(1) University College London, Department of Physics and Astronomy,
London, United Kingdom
(2) Pacific Northwest National Laboratory, Physical Sciences Division,
Richland, Washington, United States

I will discuss the mechanisms of photo-induced processes in photo-cathodes based on thin films of CsBr deposited on Cu(100). These films have been proposed as next-generation photocathode materials for applications in particle accelerators and free-electron lasers. However, the mechanisms underlying an improved photocathode performance as well as their long-term stability remain poorly understood. Our DFT calculations predict the work function reduction following the application of CsBr thin film coatings to Cu photocathodes, which explains the observed increase in quantum efficiency (QE) of coated vs. uncoated photocathodes. The effects of both flat and rough interface and van der Waals forces are examined. A model explaining the experimentally observed laser activation of photocathodes is provided whereby the photo-induced creation of Br vacancies and Cs–Br di-vacancies and their subsequent diffusion to the Cu/CsBr interface lead to a further increase in QE after a period of laser irradiation [1,2]. The desorption of Br atoms from CsBr films is induced by sub-bandgap ultraviolet radiation via an excitonic mechanism. We also provide a model of cation desorption following Franck-Hertz excitation of F-centres at the surface following irradiation of CsBr/Cu films [2]. We examine the electron trapping characteristics of low-coordinated sites at the surface, in particular di-vacancies and kink sites.

References

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[2] M. T. E. Halliday, W. P. Hess and A. L. Shluger, A mechanism of Cu work function reduction in CsBr/Cu photocathodes, Phys.Chem.Chem.Phys. 18, 7427-7434 (2016)

Hetero-phase structure and its role in photocatalysis

Zhi-Pan Liu

Fudan University, Department of Chemistry, Shanghai, China

The heterophase solid-solid junction as an important type of structure unit has wide applications for its special mechanics and electronic properties. The structure of heterophase junction is however difficult to determine for both theory and experiment. In this talk, I will first introduce our recently developed theoretical methods, namely Stochastic Surface Walking method (SSW) and Double-Ended Surface Walking (DESW) method, for resolving the reaction pathways in solid phase transition. These methods allow us to reveal the nucleation kinetics of rutile in anatase matrix and further to establish the first three-phase atomic model for anatase-rutile TiO2 heterophase junction. We then determine the optical and electronic properties of the heterophase junction, which leads to resolve the long-standing puzzles on the enhanced photocatalytic activity of anatase-rutile photocatalysts. The anatase-rutile heterophase junction has an unusual structure, containing three phases (anatase/TiO2-II/rutile), formed layer-by-layer in a “T-shape”. The intermediate TiO2-II phase, although predicted to be only a few atomic layers thick in contact with anatase, is critical to alleviate the interfacial strain and to modulate photoactivity. We demonstrate that the three-phase junction acts as a single-way-valve allowing the photogenerated hole transfer from anatase to rutile but frustrating the photoelectron flow at the opposite direction, which otherwise cannot be achieved by anatase-rutile direct junction. This new model clarifies the role of anatase, rutile and phase junction in achieving the high photoactivity synergistically and provides the theoretical basis for the design of better photocatalyst by exploiting multi-phase junction.

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Excited state dynamics in condensed matter using real time TDDFT

Sheng Meng

Chinese Academy of Sciences, Institute of Physics, Beijing, China

Laser melting of silicon has been observed for almost forty years; surprisingly, it is not well understood where most theoretical simulations show a laser-induced thermal process. First-principles nonadiabatic dynamics based on real-time time-dependent density functional theory is first employed to investigate ultrafast electron-ion coupled dynamics in laser excited silicon. With excitation conditions that account for experimental optical spectra and nonadiabatic electron-phonon effects, we observe for the first time intrinsic nonthermal melting of Si within 200 fs at temperatures far below thermal melting temperature of 1680 K. Both excitation threshold and time evolution of diffraction intensity agree well with experiment. Nonthermal melting is attributed to excitation-induced drastic changes in bonding electron density, and subsequent decrease in melting barrier, rather than lattice heating as previously assumed by the two-temperature model. We also predict that inertial dynamics can be induced by ultrafast electron-phonon energy transfer at low temperatures, not captured by plasmon annealing.

A time dependent picture of ultra-fast photo-induced charge transfer, insight from models and simulations

Cristián G. Sánchez and Dalma M. Marquez

National University of Córdoba, Department of Mathematics and Physics,
Faculty of Chemistry, Córdoba, Argentina

Since our first simulations of the real time dynamics of charge transfer in dye-semiconductor nanoparticle complexes (Negre et al, JPCL 2012, 116 (28) 14748) we have learnt some unifying characteristics of ultra-fast photo-induced charge transfer processes in a variety of systems. For dye-semiconductor complexes we where able to predict the mechanism of transfer (either type-I or type-II) and determine that illumination at different wavelengths could induce hole transfer into the valence band of the particle. We have extended those initial simulations to a variety of systems ranging from DNA-Ag complexes to non covalently bound donor-acceptor aggregates. In this talk I will give an overview of the similarities and differences between all these systems and how some insight into these processes these can be gained by modelling from simple Hamiltonians

Understanding the early stages of exciton formation and charge separation in organics

Elisa Molinari

University of Modena and Reggio Emilia, Department of Physics,
Informatics and Mathematics, Modena, Italy

Blends of conjugated polymers and fullerene derivatives are prototype systems for organic photovoltaic devices. The primary charge-generation mechanism involves a light-induced ultrafast electron transfer from the light-absorbing and electron-donating polymer to the fullerene electron acceptor. Here, we elucidate the initial quantum dynamics of this process. Experimentally, we observed coherent vibrational motion of the fullerene moiety after impulsive optical excitation of the polymer donor. Comparison with first-principle theoretical simulations evidences 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. Our 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.

Quantum mechanical modeling of nanoscale light emitting diodes

Rulin Wang (2), Yu Zhang (2), GuanHua Chen (2),
Thomas Frauenheim (3) and ChiYung Yam (1)

(1) Beijing Computational Science Research Center, Beijing, China
(2) The University of Hong Kong, Department of Chemistry, Hong Kong, China
(3) University of Bremen, Department of Physics, BCCMS, Bremen, Germany

Understanding of the electroluminescence (EL) mechanism in optoelectronic devices is imperative for further optimization of their efficiency and effectiveness. Here, a quantum mechanical approach is formulated for modeling the EL processes in nanoscale light emitting diodes (LED). Based on non-equilibrium Green's function quantum transport equations, interactions with the electromagnetic vacuum environment are included to describe electrically driven light emission in the devices. The presented framework is illustrated by numerical simulations of a silicon nanowire LED device. EL spectra of the nanowire device under different bias voltages are obtained and, more importantly, the radiation pattern and polarization of optical emission can be determined using the current approach.

Electronic excitations and photo-induced processes in van der Waals heterostructures

Kristian Sommer Thygesen

Technical University of Denmark, Department of Physics,
Kongens Lyngby, Denmark

Atomically thin two-dimensional (2D) materials have recently emerged as a new class of materials with unique electronic and optical properties. Different 2D crystals can be stacked to form “van der Waals heterostructures” (vdWH) where the individual 2D layers are held together by weak van der Waals forces leading to atomically well-defined interfaces and ensuring that the individual layers locally preserve their superior 2D properties. This fascinating scenario opens up the possibility of designing heterostructures with tailored electronic properties such as specific band structures and dielectric/optical properties. I will give a general introduction to the electronic structure of 2D materials, including the characteristic features of the dielectric function and the collective excitations in 2D materials. I will show how the dielectric function of a given 2D material can be controlled by embedding it into a vdWH, and how this in turn can be used to design the band gap, exciton binding energies, and plasmon energies. Finally, I will present recent results on the computational design of van der Waals metals for low-loss plasmonics.

Nitrogen(II) oxide charge transfer complexes on TiO_2: a new source for visible-light activity

Jana Freitag (3), Adriel Domínguez García (6,2), Thomas A. Niehaus (1),
Anja Huelsewig (5), Ralf Dillert (3), Thomas Frauenheim (2),
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(1) Claude Bernard University Lyon 1, Institute of Light and Matter, Domaine Scientifique de La Doua, Villeurbanne, France
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(6) Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Atmospheric pollution is a serious concern of society which is affecting living beings across the globe. Semiconductor photocatalysis has emerged as a very efficient and inexpensive technique to address this problem. Among the different semiconductor materials, titanium dioxide (TiO_2) is recognized as one of the most powerful photocatalysts and is often used for the purpose of air purification due to its strong oxidative ability and nontoxicity. Nevertheless, due to its wide band gap of 3.2 eV, TiO_2 absorbs only a small fraction of sunlight. Nitrogen oxides are among the most harmful atmospheric pollutant gases emitted by combustion, e.g., in stationary power (mainly coal) plants and automobile engines. There is, therefore, a great interest in reducing the concentration of these dangerous environmental pollutants.

In a joint experimental/theoretical collaboration we recently unraveled the photodecomposition of NO on TiO_2 surfaces under visible light illumination [1]. Individually, TiO_2 and NO do not absorb in the visible, while the complex experimentally shows photocatalytic activity. Theoretical simulations at the level of the TD-DFTB method [2,3] indeed revealed a absorption band in the yellow-green spectral region which corresponds to a electronic transition from the NO molecule to the semiconductor surface. This excitation weakens the N-Ti surface bond and triggers the cleavage of the NO^+ ion from the surface. Based on these results, we propose a new reaction pathway for the photocatalytic oxidation of NO.

During the talk, we will present extensions of the TD-DFTB method that were crucial for the present project. If time allows, we will also discuss the recent inclusion of range-separated functionals in the DFTB framework (LC-DFTB) [4] and first results of its time-dependent extension (TD-LC-DFTB) for electronic excited states.

References

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Electronic excitations at solid-liquid interfaces: combining GW with joint DFT

Johannes Lischner

Imperial College London, Department of Materials, London, United Kingdom

Identifying efficient systems for storing energy constitutes a major challenge in the transition to sustainable and renewable energy sources. A potential solution is to store energy in a chemical form, for example, in hydrogen gas produced by photocatalytic water splitting reactions. However, the efficiencies of current photocatalytic water splitting devices are too low for industrial applications. A detailed understanding of the electronic structure of photoelectrodes, in particular the alignment of the electrode's electronic band edge positions with the relevant redox potentials of water, is required to guide experimental progress towards increased efficiencies. To address this problem, we introduce a new approach based on the combination of many-body perturbation theory within the GW approach for the electronic structure of the photoelectrode and joint density-functional theory for the description of solid-liquid interfaces. We applied this approach to the prototypical photoelectrode material titanium dioxide and also to transition-metal dichalcogenide materials.

Solar thermal fuels: photoisomerization dynamics from TDDFT and efficiency limits for solar energy storage

David A. Strubbe (1), Jeffrey C. Grossman (2)

(1) University of California, Department of Physics, Merced, California, United States
(2) Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, Massachusetts, United States

Solar thermal fuels (STFs) are an unconventional paradigm for integrated solar-energy conversion and storage. A material absorbs sunlight and stores the energy chemically via an induced structural change, which can later be reversed to release the energy as heat. We developed and implemented a new efficient approach for TDDFT forces with the Octopus real-space code, to obtain the excited-state dynamics for promising STF molecules such as azobenzene, in agreement with available experiments. By analogy to the Shockley-Queisser limit for photovoltaics, we analyze the maximum attainable efficiency for STFs from thermodynamic considerations and assess a range of candidate molecules.

Modeling of electrochemical interfaces and processes

Timo Jacob

Ulm University, Institute of Electrochemistry,
Helmholtz-Institute Ulm, Germany

Hydrogen production through photo-induced splitting of water is a promising avenue for sustainable energy economy, although no cost-effective photocatalytic system has been identified so far. It is believed that a successful search for a new and improved photocatalyst will be based on a molecular understanding of all elementary reaction steps in the photocatalytic water splitting. Concentrating on one of the most efficient electrocatalyst for the oxygen evolution reaction (OER), RuO_2, we have investigated RuO_2 layers on TiO_2(110) single crystal substrates as model system. Though the band gap of TiO_2 is certainly too large for application purposes, here it serves as absorber material to generate the charge carriers necessary for the electrocatalytic studies on the co-catalyst. Further, this heterojunction, which is often present when using passivation layers, has a well-defined morphology due to its pseudomorphic structure and is therefore best suited to combine theory and experiment.

Combining surface science experiments and ab initio modelling we have investigated the morphology and the electronic structure of the RuO_2–TiO_2(110) heterostructures as well as the preferred surface composition that should be present under reaction conditions [1]. These investigations pave the way for in-depth studies on the mechanism of the OER on RuO_2 surfaces, which might also be relevant for other water-splitting electrocatalysts.

Afterwards, using apparently simple electrocatalytic reactions as model systems, the effects of the reactive surrounding as well as environmental parameters will be successively explored. It turns out that pure and perfect catalyst models, which are often used in literature, are in many cases insufficient.

Finally, these concepts will be extended from single crystals to the nanoregime, where nanostructured surfaces and particles are often used for electro-catalytic reactions. Taking transition metal alloys as an example, we will show that nanoparticles are not rigid objects but often change their morphologies and compositions under reaction conditions. Thus, understanding the dynamic nature of these catalysts is crucial in our efforts to further extend our ability to rationally design multi-component (electro)catalysts.

References

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The structure of titania surfaces and of initial water adsorption

Nicholas M. Harrison

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First principles thermodynamics is used to examine the equilibrium morphology of titania crystallites.

The initial adsorption of water to the rutile (110) surface is found to be significantly influenced by long range, surface mediated, inter-molecular interactions. The consequences for photocatalysis will be discussed.

In anatase the comparison of predicted morphologies to STM images of crystallite surfaces allows us to identify high index vicinal facets which contribute significantly to the surface area. Hybrid DFT calculations suggest that the photochemical response of these facets is likely to be significantly different from that of the widely studied low index surfaces.

Water splitting and the band edge positions of TiO_2

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The possibility of splitting water by UV-light on a TiO_2 electrode has created great interest in the material, however, it has been later questioned whether rutile can do the job at all without external bias. Anatase was suggested instead, but its efficiency is still a subject of debate. The problem is related to the position of the band edges, that is, of the Fermi-level (EF), with respect to the redox potentials of water. Here we present hybrid-functional calculations to align the band structures with the vacuum level, assuming the rutile (110) and anatase (101) surface being exposed to water. Our results show that both are capable of water splitting if no adsorbates other than molecular water are present. On a fully hydroxylated surface (i.e., H^+ and OH^- adsorption on undercoordinated surface oxygen and titanium atoms, respectively), EF is only ~0.5 eV above the H^+/H_2 potential in case of anatase, and – depending on the level of reduction – roughly at, or below it for rutile. We also show that the band edges (and EF) shift up if OH^+ groups dominate the surface, increasing the driving force for water splitting. This is in line with the experience on titania reduced in hydrogen. Our results are further confirmed by calculating EF without the presence of water, and comparing it to work function measurements by photoelectron spectroscopy.

Excited states of organic solids and interfaces with ab initio many-body perturbation theory

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Organic crystals are a highly tunable, diverse class of cheap-to-process materials promising for next-generation optoelectronics, such as solar cells. Further development of new organic materials requires new intuition that links molecular-scale morphology to underlying excited-state properties and phenomena. Here, I will cover the use of first-principles density functional theory – including tuned hybrid functionals – and many-body perturbation theory – within the GW approximation and the Bethe-Salpeter equation approach – for computing and understanding spectroscopic properties of selected organic crystals, including acenes from benzene to hexacene; perylene; and TIPS-pentacene. For both gas-phase and crystals, our quantitative calculations agree well with transport gaps extracted from photoemission and inverse photoemission data, and with measured polarization-dependent optical absorption spectra. We elucidate the nature of low-lying solid-state singlet and triplet neutral excitations, which have significant charge-transfer character in these systems. Implications for singlet fission are discussed. Time permitting, I will also discuss our studies of level alignment at metal-molecule interfaces, where we generalize optimally-tuned range-separated hybrid functionals to treat the electronic structure of several molecule-metal interfaces, in agreement with experiment and with accuracy comparable to many-body perturbation theory.

On the way toward efficient perovskite photovoltaics and beyond

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Present day electronic devices are enabled by design and implementation of precise interfaces that control the flow of charge carriers. Solution-processed organometallic perovskite based solar cells have emerged as a promising thin-film photovoltaic technology. Here, I will describe a novel solution-processed technique to grow high quality large-area mm-scale perovskite crystals leading to highly efficient (18%) and reproducible solar cells with reduced defect induced recombination. Theoretical simulations rationalize specifics of electronic structure of these materials, presence of interfacial states, bimolecular recombination rates and reduced losses of carriers. Ensuring photo-stability over prolonged solar irradiation a key challenge in these materials. We observe the photo-degradation and fast self-healing of the photocurrent in perovskite solar cells under constant illumination. We attribute the photocurrent degradation to the formation of light-activated small polaron trap states. Experimental characterization and theory suggest their origin to the formation of localized charged states strongly coupled with local structural lattice distortions and methyl ammonium (MA) quasistatic configurations. Finally, I outline results on 2D layered hybrid perovskite, which was incorporated into a photovoltaic device that exhibited a world-record efficiency (13% in the category of 2D materials) and stability for over 3 month under constant light illumination and 65% humidity. Overall, our results provide insight towards the material design for efficient and photo-stable perovskite solar cells.

Impact of static and dynamic disorder on charge recombination in organic solar cells

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We study the role of electron-vibration coupling, electronic polarization, molecular packing, system size and electron delocalization on the nature of the charge-transfer states in model donor-acceptor systems. The morphologies range from a bilayer with flat interface to bulk heterojunctions with coarse and fine intercalated domains of donor and acceptor molecules. The implications of the charge-transfer states, active material morphology, density of states and charge carrier concentration on non-geminate recombination kinetics is investigated by means of a three-dimensional reaction-diffusion lattice model with the charge carrier hopping rate described by the Miller-Abrahams formalism.

QM/MM studies of excited state non-radiative decay and charge mobility in molecular aggregates

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Excited state non-radiative decay rate is one of the most important quantity to evaluate, posing great challenge. We combine both non-adiabatic coupling and spin-orbit coupling terms in Fermi-Golden rule to develope a first-principle formalism to calculate the photophysical preperties and optical spectra for molecules and aggregate. The exotic aggregation-induced emission phenomena is unravelled [1]. The same formalism is also applied to understand the charge transport phenomena in organic semiconductors. The quantum nuclear tunneling versus charge localization effects are demonstrated [2].

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Electronic processes at organic-(in)organic interfaces

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We will review recent work on the modeling of electronic processes going on: (i) at molecular interfaces between electron-rich and electron-poor organic conjugated molecules used to promote either photoinduced excited-state charge separation in photoconversion layers or ground-state charge transfer (doping) in electrically conducting layers; and (ii) at planar interfaces between organic electron-extracting and lead halide perovskite layers for photovoltaics. In both cases, we will highlight how the detailed microstructure affects charge transfer and hybridization at the interface and the resulting energy level alignment.

Excited state phenomena and photo-physics of atomically thin 2D materials

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Atomically thin quasi two-dimensional (2D) materials and their nanostructures can exhibit highly unusual behaviors. Owing to their reduced dimensionality, these systems present opportunities for manifestation of concepts and phenomena that may not be so prominent or have not been seen in bulk materials. Symmetry, many-body interaction, doping, and substrate screening effects typically play a critical role in shaping qualitatively and quantitatively their properties, and thus their potential for applications. Accurate treatment of these effects, in particular many-electron interactions, in quasi 2D materials poses new theoretical and computational challenges. In this talk, we present some first-principles studies on monolayer and few-layer transition metal dichalcogenides and metal monochalcogenides, as well as black phosphorus and other 2D crystals. Several highly interesting and unexpected phenomena are discussed: novel exciton behaviors; tunable transport, optical, magnetic and plasmonic properties; and the dominant influence of substrate screening.

Non-adiabatic dynamics of charge and energy transfer at nanoscale interfaces

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Photo-induced processes at interfaces are key to photovoltaic and photo-catalytic applications. They require understanding of dynamical response of novel materials on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques, implemented within time-dependent density functional theory, allow us to model such non-equilibrium response in real time. The talk will focus on photo-initiated charge and energy transfer at interfaces involving several classes of nanoscale materials. Examples include TiO_2 sensitized with organic molecules, water, semiconductor quantum dots, graphene and perovskites, a GaN/water interface, carbon nanotube bundles, mixtures of C_{60} with inorganic particles, etc. Photo-induced charge separation and recombination across such interfaces creates many challenges due to stark differences between molecular and periodic, and organic and inorganic systems. Our simulations provide a unifying description of quantum dynamics on nanoscale, characterize the rates and branching ratios of competing processes, resolve debated issues, and generate theoretical guidelines for development of novel systems for solar energy harvesting.

Light-matter coupling in density-functional theory for quantum electrodynamics

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Recently time-dependent density-functional theory has been extended to include the interaction with photons from first principles. This so-called quantum-electrodynamical density-functional theory (QEDFT) treats light and matter on equal quantized footing and provides a bridge between quantum chemistry and quantum optics. In the first part of the talk, we illustrate effects that appear in the strong-coupling regime of matter with cavity photons. In particular, we show how Born-Oppenheimer surfaces are modified by the presence of the cavity and analyze how molecular spectra are modified. In the second part, we focus on a description of light-matter coupling within QEDFT. We show for a quantum dot system the exact time evolution of the effective potential of the Maxwell-Kohn-Sham system in QEDFT and analyze this in terms of a cavity Born-Oppenheimer approximation. We compare these exact results with an optimized-effective-potential approach for the coupled matter-photon system and present real-time propagations of the coupled Maxwell-Kohn-Sham equations for molecular systems.

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Exciton dynamics in organic and perovskite photovoltaics – a large-scale TDDFT study

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Exciton dynamics is at the heart of emerging photovoltaic technology employing both organic and inorganic perovskite based materials. Time-dependent density functional theory (TDDFT) has become one of the most powerful and versatile tools to probe exciton dynamics in these materials. Unfortunately, TDDFT is computationally demanding and as a result, its application to realistic materials remains exceedingly difficult. In this talk, I will outline our recent progress in developing accurate and efficient TDDFT methods that would allow us to start addressing these challenges. Among them, a subspace TDDFT method is developed which can calculate both excitation energy and excited state forces accurately for systems containing up to a few thousand electrons. Combining the TDDFT methods with non-adiabatic molecular dynamics, one can perform coupled electron-ion and exciton-ion dynamics where phonons are important in electron transitions and excitations. I'll show how these first-principles methods can be brought upon to examine exciton dynamics such as spontaneous electron-hole separation and charge stripe formation in perovskite solar cells as well as exciton diffusion in disordered semiconductors for organic photovoltaics.

Affordable first-principles modeling of charge transport: where did my holes go?

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In organic electronics, charge carrier mobility is a key performance parameter. Due to the complex manufacturing processes of e.g. organic field effect transistors (OFETs) measured mobilities are often heavily affected by the device preparation. This masks the intrinsic materials properties and therewith hampers the decision whether further device optimization for a given organic molecule is worthwhile or not. We developed a fast and efficient protocol with a descriptor based on electronic coupling values to assess the expected performance of organic materials for application in organic electronic devices. Applying this protocol to experimental structures of organic crystals obtained from the Cambridge Structural Database (CSD), we screened about 40000 structures employing only first principle methods. Out of the 28000 successfully calculated structures we selected 2000 candidates with above average electronic couplings for additional calculations and in-depth analysis using statistical methods and automated classification based on chemical structure. This allowed us not only to identify a number of specific crystals with exceptionally high electronic coupling values and therefore promising properties, but also possible lead structures which can be the basis for in-depth theoretical and experimental studies of new classes of materials for organic electronics.

Excitonic quasiparticles in TiO_2

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TiO_2 is a widely employed material for photocatalytic applications. Many researchers have exhaustively studied its surface properties in order to improve its ability to assist different photo-reactions. However, the nature of its fundamental charge excitations is still unknown and its investigation requires both experimental and theoretical efforts. This bulk property is of high relevance for the deep understanding of TiO_2 photocatalysis. In my talk, I will present and discuss our most recents findings on the excitonic characteristics of both the rutile and anatase polymorphs of TiO_2, using state-of-the-art theoretical calculations and advance steady-state and ultra-fast spectroscopies. I will show that for anatase, the direct optical gap is dominated by a strongly bound exciton with a two-dimensional character. Possible connections between the nature of this exciton and the enhanced photocatalytic activity of the anatase TiO_2 (001) facet will be addressed. Importantly for light-energy conversion applications, I will show that our results also apply to defect-rich samples.

Abstracts of Posters

In silico characterization of polymer-fullerene organic photovoltaic bulk heterojunctions

P01

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Organic solar cells (OSCs) are among the new generation photovoltaic technologies which could be employed to convert solar energy. The most efficient OSCs fabricated to date require a bulk heterojunction, an active layer composed of intimately intermixed electron acceptors – molecules with a high electron affinity such as fullerene derivatives – and electron donors – such as semiconducting polymers. The morphology of this layer has been shown to be crucial for the efficiency of the device because of its decisive impact on the charge separation process. However, a fundamental understanding of the relationship between morphology, electronic properties and efficiency is still sought after.

Coarse-grain (CG) models compatible with the Martini CG force field [1] are used to generate morphologies via large-scale solvent evaporation simulations [2], allowing the study of the morphology as a function of the structure of the molecules. These CG morphologies are then back-mapped to atomistic resolution. The electronic structure of molecules at the interfaces and in the bulk is determined with quantum chemical (QC) calculations. Particular attention is given to the distribution of microscopic properties (excited state energies, local dielectric response, Fig. 1) and how these impact macroscopic properties (exciton binding energy, dielectric constant) and the charge separation process.

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Calculating the electronic band edges at TiO_2/water interfaces **P02**

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Identifying efficient systems for storing energy constitutes a major challenge in the transition to sustainable and renewable energy sources. A potential solution is to store energy in a chemical form, for example, in hydrogen gas produced by photoelectrolytic water splitting [1]. However, the efficiencies of current photoelectrolytic water splitting devices are too low for industrial applications. A detailed understanding of the electronic structure of photoelectrodes, in particular the alignment of the electrodes' electronic band edge positions with the relevant redox potentials of water, is required to guide experimental progress towards increased efficiencies. To address this problem, we introduce a new approach based on the combination of many-body perturbation theory within the GW method [2] for the electronic structure of the photoelectrode and joint density functional theory [3,4] for the description of solid-liquid interfaces. We applied this approach to the prototypical photoelectrode material titanium dioxide, both in the rutile and anatase phases, and determined the position of the valence and conduction band edges with respect to the redox potentials associated with the hydrogen and oxygen evolution reactions. Future work will compare the accuracy of implicit solvent models, such as joint density functional theory, to ab initio molecular dynamics simulations of solid-liquid interfaces.

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Many body perturbation theory on lead candidates for high-performance organic photovoltaics

P03

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In organic photovoltaic (OPV) cells, the photocurrent generation efficiency depends critically on charge–separation (CS) of the electron-hole (exciton) at the interface between electron donor and acceptor phases. This CS process depends on charge transfer (CT) effects taking place at the donor–acceptor interface. In order to theoretically devise new OPV cells with high efficiency, it is thus important to describe these CT effects adequately. In this framework, the Green's function based many-body perturbation theory (MBPT) constitutes a choice tool for computing the electronic and optical properties of materials [1]. Since the mid-80s, this approach has proven very accurate for extended semiconductors. In particular, the so-called GW/BSE formalism correctly reproduces experimental electronic and optical band gap in many studied systems. Recently, an efficient "auxiliary Gaussian basis" implementation of the GW/BSE formalism (the Fiesta code [2]) has been developed allowing to treat molecular systems consisting of up to a few hundred atoms.

The present project aims at studying the electronic and optical properties of the interface between various theoretically designed donors and an acceptor (fullerene C60) using the Fiesta code. Tens of thousands of molecules have been already tested in a multiple-step screening within the Harvard Clean Energy Project (CEP) [3], leading to a ranking of potential candidates for efficient organic photovoltaics. However, the calculations have been performed relying on density-functional theory which is known to underestimate the band gap and not to describe electron-hole interaction and CT effects correctly. Here, we focused on the top 21 donor molecules from the CEP ranking. In a first step, we computed the electronic and optical properties for the donor alone. In a second step, we considered the complete fullerene-donor complexes and computed highly accurate band gaps, exciton binding and charge-transfer energies. The Harvard group computed the equilibrium geometries of the complexes and the UCL team carried out the corresponding GW/BSE calculations. From these results, we were able to evaluate possible efficiency loss pathways.

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Three-particle correlation from a many-body perspective: trions in a carbon nanotube

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Trion states of three correlated particles (e.g., two electrons and one hole) are essential to understand the optical spectra of doped or gated nanostructures, like carbon nanotubes or transition-metal dichalcogenides. We develop a theoretical many-body description for such correlated states using an ab-initio approach [1]. It can be regarded as an extension of the widely used GW method and Bethe-Salpeter equation, thus allowing for a direct comparison with excitons. We apply this method to a semiconducting (8,0) carbon nanotube, and find that the lowest optically active trions are red-shifted by ~130 meV compared to the excitons, confirming experimental findings for similar tubes. Moreover, our method provides detailed insights in the physical nature of trion states. In the prototypical carbon nanotube we find a variety of different excitations, discuss the spectra, energy compositions, and correlated wave functions.

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2D-materials-based sensing in liquid solvents: effects of polar and non-polar solvents on the vibrational and electronic properties

P05

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2D-materials such as graphene and transition metal dichalcogenides (TMDC) (MX2 , e. g. MoS2) have been proposed as active sensing elements for inorganic molecules and biomolecules. Embedded in field-effect transistor devices, they show a high sensitivity and selectivity for the detection of dissolved molecules such as mercury ions, cocaine, nucleotides, etc. at concentrations as low as 1pM. A shift of the transition point between the hole-mobility- dominated and electron-mobility-dominated regimes in the gate voltage vs drain current (Dirac voltage) can be observed in the 2D-material, induced by surface-adsorbed molecules. These cause a perturbation of the electron density distribution in the sheet, in turn mediated by the solvent, which affects the transport properties. This poster shows preliminary results in the theoretical investigation on how graphene or TMDC 2D-materials interact with different solvents (polar, non-polar, ionic etc.), and especially on how such interactions affect their transport properties. Polarization patterns, the shift of phonon frequencies and the change of the interfacial structures induced by molecular adsorption in different liquid environments (water, ethanol, benzene etc.) are reported.

An adaptive sparse grid approach for quantifying the error propagation in first principles based (photo-) catalytic kinetic models

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First principles kinetic Monte Carlo (1p-kMC) models utilize Density Functional Theory (DFT) based rate constants (RCs) as the input for mesoscopic reactivity models. Despite the success of DFT, the employed approximations can easily lead to uncertainties in the RCs of two or more orders of magnitude. We quantify the error propagation to the kinetic simulation results by a global sensitivity analysis (GSA), i.e. we decompose the error in the result into contributions caused by each uncertain RC. The required high dimensional integrals over the space of the RCs are numerically evaluated using locally and dimension-adaptive sparse grids. With this approach, we can exploit that, typically, strongly non-linear behaviour only appears in small sub-domains (local adaptivity) and on low-dimensional subspaces (dimension-adaptivity) of the whole parameter space. As a prototypical example, we consider the first-principles kinetic Monte Carlo model for the CO oxidation on a RuO_2(110) surface and discuss the extension to photocatalytic kinetic models. Besides a qualified discussion of the effect of the modelling error, the approach can be employed for the reduction of the number of expensive first-principles simulations or the identification of descriptor sets in computational materials screening.

Band-gap and binding-energy renormalizations due to excited carriers in monolayer TMDs

P07

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Atomically thin layers of transition-metal dichalcogenides are an intriguing class of material systems. Indirect in the bulk, as monolayer MoS2, MoSe2, WS2, and WSe2 possess a direct band. Excitonic properties are additionally defined by the Coulomb interaction between charge carriers in the band structure, which has been shown to be exceptionally large due to the weak screening in the thin layer itself.

The poster presents results on excited-state optical properties of the typical monolayer TMDs. Excitonic resonances have been shown to shift in absolute value and relative to each other with increasing carrier density [1,2]. The effect is a result of a band-gap reduction due to many-particle renormalisations, and a reduction of the binding energy due to screening of the Coulomb interaction, which we analyse and compare in detail for MoS2, MoSe2, WS2, and WSe2.

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Carrier dynamics in transition metal dichalcogenides P08

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In the context of the current interest in devices based on transition-metal dichalcogenides, we study the optical generation and relaxation of excited carriers. In these two-dimensional atomically thin semiconductors, the Coulomb interaction is known to be much stronger than in quantum wells of conventional semiconductors like GaAs, as witnessed by the up to 50 times larger exciton binding energy. The question arises, whether this directly translates into equivalently faster carrier-carrier Coulomb scattering of excited carriers. We answer this question by combining ab-initio information about the band structure and the single-particle wave functions with kinetic equations for the Coulomb-induced carrier scattering in the full Brillouin zone [1]. Our results yield carrier scattering only a factor of 3-4 faster than in GaAs QWs. The carrier-carrier Coulomb scattering indicates a sub-100fs carrier relaxation dynamics leading to ultrafast carrier population in different valleys of the band structure.

The other main source of carrier relaxation is the interaction of the excited electrons and holes with phonons. To analyze carrier-phonon scattering, we solve kinetic equations, based on ab-initio carrier-phonon interaction matrix elements, both for carriers and phonons, thereby including heating effects due to the excitation of non-equilibrium phonons. We find that within 100fs the electrons have relaxed from the excitation into the valleys, demostrating fast carrier dynamics, which is accompanied by the generation of non-equilibrium phonons. This process is followed by carrier cooling on a timescale of about 1ps, which is consistent with recent experimental findings [2,3].

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Calculating surface charge trapping with the help of the Lany-Zunger polaron correction

P09

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Photocatalysis is one of the most important applications of photo-induced processes on solid surfaces in which electrons and holes are generated by absorption of photons with higher energy than the semiconductor band gap. Charged species resulting from photo-excitation may get trapped on the surface of the photocatalysts and consequently transferred to adsorbed species on the surface, promoting specific reactions. Therefore, in modeling such processes, it is crucial to have a method which correctly describes charge trapping on surfaces. The standard local or semi-local implementations of density functional theory (DFT) have the tendency for delocalization of the wavefunction, and self-trapping in small polaron states, which often occur in oxides used for photocatalysis, cannot be reproduced. Hybrid functionals can solve this problem but in periodic slab models these are computationally too expensive. A convenient solution for solving the band-gap and charge delocalization problem is to apply the corrections suggested by Lany and Zunger in a generalized gradient approximation (GGA) calculation. This method works well for bulk systems, but due to the different screening in the environment of under-coordinated atoms on the surface, the standard correction fails for slab models. Here we show that by making the atom- and angular-momentum dependent correction parameters of Lany and Zunger also coordination dependent, it is possible to correctly describe the trapping of charge carriers in small polaron states on the anatase (101) surface at a relatively low computational cost.

Ultrafast excitonic processes in organic conjugated materials

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Excitons and polarons are the major players in governing energy and charge transfer phenomena in soft materials [1]. They are the primary outcome of light-matter interactions.

Our understanding about their formation and relaxation mechanisms has significantly improved, however several features are still obscure. For instance, there is not a clear comprehension yet about the high-energy ultrafast exciton relaxations in complex molecular systems, leading to polaron formation/recombination phenomena.

In this contribution, via time dependent density function theory (TD-DFT) calculations and surface hopping techniques [2,3], we get mechanistic insights into three processes: 1) ultrafast exciton relaxations and charge transfer dynamics [2,3], 2) singlet-triplet excitons dynamics and spin-orbit coupling mechanisms [4], 3) polarons generation and their spectroscopic signatures [5].

A survey of the above processes over different classes of organic materials is presented, spanning from thiophene-based molecules vs. aggregates, homo- vs. low band gap co-polymers (e.g. P3HT vs. C- and Si-PCPDTBT), and donor/acceptor interfaces.

Fundamental mechanisms are tackled and critically discussed, proposing molecular design rules to effectively improve the light-to-current conversion efficiency in functional organic materials.

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Study of electron transport in organic molecules using constrained density functional theory

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Photocurrent generation in organic photovoltaics (OPVs) relies on the dissociation of the excitons into free electrons and holes at donor/acceptor heterointerfaces. The low dielectric constant of organic semiconductors leads to strong Coulomb interactions between electron-hole pairs that should in principle oppose the generation of free charges. The exact mechanism by which electrons and holes overcome this Coulomb trapping is still unclear. In our work, we try to better understand theoretically the charge transport mechanisms at the atomic scale. Single donor/acceptor pairs may be trapped in cold hydrogen or rare-gas matrix, where spectra can be recorded in unprecedented precision. We aim to look precisely into the vibronic transitions important in CT excitons in heterocyclic benzene molecules as their fingerprints and hence make use of quantum chemical ab-initio methods such as density functional theory for describing the ground state of the system. Using time-dependent DFT might indicates changes in electronic distribution of molecular excited states, however for a precise study of energetics a powerful theory is needed to be able to describe electrons not only in their excited states but also in continuum. To accomplish our aim we consider Constrained DFT[1] to discover the CT states in n-benzene rings molecules.

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Apprehending chemical processes in ALD and rationalising the selection of precursors: the numerical way

P12

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Atomic Layer Deposition (ALD) is a technique that is used to grow thin uniform films even on substrates with a high aspect ratio, with a fine control of composition and thickness. Reactive species called precursor and coreactant are alternatively pulsed and self-limiting surface reactions take place. ALD has applications not only in photovoltaics but also in microelectronics, coatings, etc. Materials deposited through ALD are mostly metal oxides, nitrides or chalcogenides. Here we propose a case study with a sulfide material: Gallium sulfide. We want to describe the growth of this material in ALD conditions at the atomic scale.

Ab initio modelisation has proven a power tool in both (i) the selection of precursors and (ii) the rationalization (including kinetic and thermodynamic properties) and prediction of ALD reaction mechanisms. In our work, numerical methods (DFT) are used to characterise the stability and reactivity of a series of precursors and to shed light on a network of reactions that may take place on a Ga2S3 surface, exposed a precursor/coreactant couple: Ga(NMe2)3/H2S. A cluster model is proposed to describe the growing material.

This ongoing study confirms some experimental observations: (i) amorphous character of the growth, (ii) by-products trapped at the surface. New elements can be given: (iii) Structures and relative energies of key intermediates and transition states, (iv) role of side-reactions, (v) role of coreactant H2S, (vi) role of eventual (e.g. oxygen) impurities at the surface. Upon completion of this study, by injecting a set of relevant energy barriers obtained from our DFT calculations into a kinetic model, it will become possible to simulate the evolution of deposition of the material as a function of time.

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Studying water-CdS surfaces interactions from first-principles DFT P13

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It is about five decades since it was realized that small band-gap semiconductors can serve as efficient photocatalysts for water splitting. However it is only in the last decade, with the developments in synthesis of nanoheterostructures, that they have re-assumed the promise of hydrogen fuel applications. Among these semiconductors, CdS is one of the most widely studied. We simulated the adsorption of water molecules and water monolayers on key CdS surfaces, using first principles density functional theory (DFT) employing a van der Waals exchange-correlation functional. We also investigated the effect of vacancy- defects at the surface, which often exhibit magnetism in the case of II-VI semiconductors, on the water-surface interaction – and found that they have a significant effect on water adsorption and possible dissociation processes.

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Exciton effect in graphdiyne nanotubes

P14

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We present a theoretical study of the electronic and optical properties of graphdiyne-based nanotubes (GDNT). These semiconducting nanotubes result from the elongation of one-third of the covalent interconnections of graphite-based nanotubes by the introduction of yne groups. In the present investigation, the electronic, structural and optical properties of GDNTs having different diameters have been studied systematically. We predict the structural and optical properties of GDNTs and influence of different chirality on these properties. All different studied chirality (armchair and zigzag edges) were studied by using BSE/DFT calculations. The GDNTs display properties of semiconductor. Band structure of GDNTs shows that the magnitude of band gap is in close range (between 0.25 and 1 eV). The cohesive energies of GDNTs indicate that these carbon nanotubes are more stable than conventional carbon nanotubes with the same diameters. Optical spectrums of the GDNTs show that the exciton binding energies are anomalously large at about ~1 eV.

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Large-scale simulations of reactive nano particles

P15

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We have explored the stability and energetics of reactive oxygen species (ROS) and how they may form on the surface and bulk of ceria [1] and on small models of ceria nano particles (CNPs) [2]. Our Density functional theory (DFT) calculations shows that cerium rich, and hence partially reduced, CNP’s are stabilized in oxidative atmosphere through a strong interaction with oxygen molecules leading to the formation of superoxide species residing at the surface. This in turn results in oxygen rich particles, supercharged CNPs, which explain the dramatically increased oxygen storage capacity (OSC) found for small CNP’s. Recent experimental findings [3] provide support for our proposed mechanism. Besides the increased OSC for small CNP’s, the large amount of ROS opens up for low-temperature redox chemistry without the formation of explicit oxygen vacancies, a process associated with high energy barriers. I will present our current understanding of supercharging in CNP's, based on our previous DFT calculations on simple model structures and show how self-consistent charge density functional tight binding (SCC-DFTB) can be used to study more complex structures.

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Ab initio study of electron-phonon coupling in metal-adsorbate systems

P16

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Plasmon-induced chemical reactions on metallic nanoparticles are gaining significant attention since they provide a platform to utilize sunlight as a renewable source of energy. In order to efficiently design such catalytic systems, it is important to understand and control (1) the coupling of plasmons (or photons) to hot carriers, and (2) the coupling of generated hot carriers to the adsorbates. We present an ab initio study of the latter process based on density functional theory calculations. Our analysis, based on several adsorbates and metallic substrates, reveals different parameters that could be controlled to efficiently transfer energy from hot carriers to adsorbate molecules. Thus, we envision our computations to provide theoretical guidelines to design more efficient photocatalytic systems.

Band alignment and interlayer excitons in van der Waals heterostructures

P17

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Due to their extraordinary (opto)electronic properties, the use of van der Waals Heterostructures (vdWHs) in high-performance (opto)electronic devices is now well established. Stacking two-dimensional (2D) layers in vdWHs not only allows us to combine and tune the properties of the constituent layers, but it also leads to the formation of interfaces where new physical phenomena take place. For example, vdWHs are ideal hosts of electron-hole pair excitations where the electron and hole are localized in distinct layers, namely interlayer excitons. It is well understood, that the spatial separation between the electron and the hole in an interlayer exciton relies on an underlying type-II electronic band alignment between the layers hosting the two charges. As a consequence of the spatial charge separation, the interaction energy between the electron and the hole is less strong, resulting in interlayer excitons with a lower binding energy than their intralayer counterpart and therefore more prone to dissociation. This represents a key feature in (opto)electronic devices, such as solar cells, where efficient charge dissociation at the interface is necessary. As a first step towards device engineering is thus crucial to accurately describe the electronic and excitonic level positioning in vdWHs. However, the application of standard ab-initio methods is limited to commensurable van der Waals stacks consisting of a few layers. In our work we show how to overcome these limitations, by means of our recent developed multi-scale method, the quantum electrostatic heterostructure (QEH) approach, where the electronic properties of the individual layers are computed ab-initio and then coupled together via the long-range Coulomb interaction. In other words, interlayer exciton binding energies and electronic band alignment in vdWHs can be accurately calculated directly from the monolayers building blocks, without having to perform calculations for the full structure. In the case of excitons this is done by first using the QEH to calculate the screened electron-hole interaction and then employing a generalized Mott-Wannier model to compute exciton binding energies. For the electronic excitations we use the QEH to modify standard G0W0 calculations of isolated layers in order to include the effect of interlayer dielectric screening on the electronic bands. Remarkably we are able to predict band positioning in a vdWH at the cost of, at most, N-G0W0 monolayer calculations, with N the number of layers in the stack. We present actual calculations for interlayer excitons and band alignment for MoS2-WSe2 heterostructures intercalated with hBN. The validity of our approach is then tested by comparing this results to available experimental data on interlayer excitons photoluminescence peaks.

In silico high-throughput screening of non-fullerene acceptor materials for applications of organic photovoltaic devices: a Harvard Clean Energy Project study

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Organic Photovoltaics (OPVs) have shown a steady growth in efficiencies since the 1980s, and reported percent conversion efficiencies (PCEs) up to 12% are reported in multi-junction cells. OPVs are lightweight, easy to produce, and feature chemically diverse components. While PCBM is the standard fullerene n-type (acceptor) material, it is not without limitations, which include limited spectral breadth, small range of LUMO energies, and relatively high costs of industrial production. We have undertaken an in silico high-throughput screening utilizing the Harvard Clean Energy Project to explore the chemical space associated with non-fullerene acceptor materials. A library of 100,000 n-type materials including perylene diimides, tetraazabenzodifluoroanthenes, diketopyropyrroles, and fluoroanthene-fused imides. A smaller secondary screening of hexabenzocoronenes has identified novel non-fullerene acceptor materials for OPVs. The predicted donor/acceptor pairs will be presented and their experimental performance compared to traditional donor-fullerene OPVs.

Theory-experiment approach identifies new directions for contorted electron donor and acceptor materials for organic photovoltaics

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Earth receives several orders of magnitude more in solar energy than the current global energy demand. An array of photovoltaic technologies is needed to utilize this vast resource; thin-film organic photovoltaics (OPVs),made from low-cost carbon-based materials, are finding use in building-integrated PV (BIPV) systems, flexible power generation systems and many other niche markets. OPV devices require a donor and an acceptor material to facilitate exciton dissociation into free charge carriers. In this work we explored the chemical space of contorted hexabenzocorones (cHBC) derivatives because of their chemical stability and highly-tunable optoelectronic properties. Recently, the Loo group (Princeton University) demonstrated that these electron donating materials could be converted into electron accepting materials via halogenation of the molecule's peripheral aromatic moieties. We utilized quantum mechanical calculations using density functional theory (DFT) to evaluate the electronic structure of contorted electron donor and acceptor materials to guide the next generation of materials using the combined expertise of our groups. We computed the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) using B3LYP/6-311G(d,p)-IEFPCM=4–D3BJ//B97D/6-31G(d,p), along with the excitation energies (and absorbance spectra) using TD-B3LYP/6-31G(d,p)–IEFPCM=4–D3BJ. Drawing on this data, we identified novel cHBC derivatives and donor-acceptor pairs well-suited for BIPVs, ultraviolet sensors, and solar-power water splitting; synthesis of the most promising candidates is currently underway.

Density functional theory – TDDFT study of interfacial charge transfer complexes of 2-anthroic acid and TiO_2 nanoparticles

P20

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Surface complexes of 2-anthroic acid and titania show the formation of an interfacial charge transfer band and are promising for dye-sensitized solar cells with direct injection. We present a comparative density functional theory modelling of the adsorption of 2-anthroic acid on a TiO_2 nanocluster exhibiting a (101)-like interface using a GGA functional and a hybrid functional. We compute light absorption properties of this system and confirm the formation of interfacial charge transfer bands. We also show that the often used strategy of using a lower level of theory to optimize the geometry followed by single point calculations of adsorption or optical properties introduces significant errors which have been underappreciated: by up to 3 eV in adsorption energies, by up to 5 times in light absorption intensity, as well as absorption peak maxima shifts by dozen nm.

Band alignment between a large molecule and an oxide: DFTB advantage in accuracy not just speed

P21

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We show that for big molecules such as biomolecules, Density Functinal Tight Bindings (DFTB) not only enables routine approximate ab initio modeling due to its cpu cost advantage, but can be preferred also for accuracy. Hybrid functionals remain and will likely remain for some time prohibitively costly for modeling of bioinorganic interfaces; while GGA remains viable albeit costly. I will show that there is a qualitative difference between a small and a big molecule adsorption on a semiconductor, in that the HOMO of a big molecule can enter the conduction band leading to a qualitatively wrong picture with GGA DFT. This effect has been under-appreciated due to the frequent use of abridged models of biomolecular adsorption. DFTB, which can effectively reproduce the band gap, avoids this problem and can provide qualitatively or quantitatively correct interfacial band structure and adsorption properties.

Theory of charge transfer at the TiO_2-graphene interface

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Long-lived electrons and holes are among the main requirements for efficient photocatalysts. To achieve this, the recombination of electrons and holes should be suppressed. One of the ways to avoid this recombination is the use of charge-transfer interfaces. TiO_2-nanocarbon composites, in particular TiO_2-graphene interfaces, have shown better photocatalytic properties than pure TiO_2; this has been attributed to electron-hole separation at this interface [1]. However, charge transfer at this interface has not yet been well understood: theory has described the role of graphene as a photosensitiser [2,3], but not its role as an electron acceptor. This work investigates electronic properties of the TiO_2-graphene interface to understand the behaviour of graphene as electron acceptor.

We use density-functional theory (DFT) calculations using the hybrid HSE06 functional to model the commensurate rutile (110)/graphene interface. An accurate computational model (hybrid DFT and a dense k-point grid) is essential for a reliable description of this system. We confirm that rutile (110) and graphene interact by physisorption and graphene remains semimetallic; at the same time, there is mixing of TiO2 and graphene states below the conduction band of TiO_2. We find essentially no electron transfer in this system in its ground state. However, the Fermi level of graphene remains below the conduction band of TiO_2, therefore, photoexcited TiO_2 will donate electrons to graphene. Therefore, our calculations show that graphene acts as electron acceptor in the TiO_2-graphene interface.

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Structure and thermodynamic, electronic and spectral properties of photocatalysts based on the TiO2/HEMA nanocomposites
A DFT and DFTB study

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Materials based on titanium dioxide and its derivatives (poly-TiO2 gels, hydrated titanium dioxide, solid state copolymers) are considered today as the most promising photocatalytic systems. Their catalytic activity is provided due to the electronic properties of TiO2¬¬-materials, which are based on UV-induced reversible one-electron transition Ti4+ + e → Ti3+. This process leads to the formation of active sites which exhibit catalytic properties of oxidation reactions useful in oxidation of various organic and inorganic environment contaminants and in organic synthesis. Other applications of such materials are solar cells, photoelectrochromic materials and chemical sensors. Recently, a new promising photocatalytic material – the optically transparent solid state organic-inorganic copolymer TiO2/HEMA (HEMA – hydroxyethyl methacrylate) doped by Au or Ag nanoparticles – was synthesized [1]. Such copolymer contains (TiO2)poly nanostructures incorporated in organic polymer matrix with the coordinated nanoparticles of noble metals working as a trap for photons and expanding the light absorption range. The molecular structure of such materials has a strong influence on the properties of the material and defines the area of their further use. The key issue for the development of photocatalytic materials is the question about structure of the solid hybrid copolymers and its influence on the mechanism and characteristics of the photocatalytic activity. In the current study we performed the quantum chemical calculations on structure and properties of oxo-carboxy-titanium clusters [TinOm(OEt)k(OEMA)l] as models of the TiO2 nanoclusters incorporated into the organic network. The photosensitive sites were modeled by the Au atoms and Au7 clusters coordinated on TiO2 sites of various structure using the DFT theory at the B3LYP/6-31G(d,p)/LANL08(Au) level. Extended organo-inorganic clusters were studied with the SCC-DFTB [2] theory using the Ti parameters developed in [3]. On the basis of comparison between the calculated spectra of clusters of a various structure and experimental data, the characteristic structural motifs of TiO2/HEMA copolymers were established. The photoexcitations were considered using the TD-DFT theory and the photochemical characteristics of TiO2/HEMA were estimated and compared with the measured ones. On this basis, the mechanisms of electron transfer due to the photoexcitation are analyzed.

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This work was supported by the RFBR (Project No. 14-03-00585)

Excitons and optical spectra of phosphorene nanoribbons

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On the basis of many-body {\it ab-initio} calculations, using single-shot G_0W_0 method and Bethe-Salpeter equation, we study phosphorene nanoribbons (PNRs) in the two typical zigzag and armchair directions. The electronic structure, optical absorption, electron-hole (exciton) binding energy, exciton exchange splitting, and exciton wave functions are calculated for different size of PNRs. The typically strong splitting between singlet and triplet excitonic states make PNRs favorable systems for optoelectronic applications.

Quantum confinement occurs in both kinds of PNRs, and it is stronger in the zPNRs, behave like quasi-zero-dimensional systems. Scaling laws are investigated for the size-dependent behaviors of PNRs. The first bright excitonic state in PNRs is explored in detail.

Multi-excitons Auger recombination in single-walled carbon nanotubes

P25

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Generation of multiple electron−hole pairs by single photon or carrier multiplication (CM) in nanosystems are at the heart of fundamental studies as well as conceivable applications for high efficiency generation-III photovoltaics. The inverse of CM is Auger recombination which plays an important role in determining exciton dynamics in these nano systems. In semiconductor materials, Auger processes opens up a new nonradiative recombination channel (Auger recombination) in which the electron-hole (e-h) recombination energy is transferred to a third particle (an electron and or a hole) that is excited to a higher-energy state. Herein, we present a comprehensive study of multiparticle Auger recombination in SWCNT with a range of aspect ratios. Our results reveal a systematic relationship between the biexciton (τ2) and triexciton auger lifetime (τ3) of the chiral carbon nanotube. Specifically, for a fixed diameter (d), τ2 and τ3 increase with increasing aspect ratio of the chiral SWCNT. Our analysis also indicates that with increasing the aspect ratio of the tube, the rate of increment for both τ2 and τ3 deceases and that will be more for τ3 than τ2. Nevertheless, the observed enhancement of the multiparticle auger lifetime is quite considerable, exploring the underlying physics of aspect ratio dependent multiparticle auger life time in SWCNT, which in turn gives us the idea that the control of aspect ratio would be a promising approach to enhance the multiple exciton generation in SWCNT. Our simulation also reveals that aspect ratio dependent auger lifetime purely depends on the coulomb coupling. Such control of auger decay rates for higher multiparticle states, increases optical-gain lifetimes or optical efficiency, and to extend the gain region into the range of high-energy transitions involving excited electronic states.

DFT simulations of the electronic energy level alignment

P26

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The advantageous energetics of the frontier electronic levels of the CH3NH3PbI3 perovskite is one of the key properties at the basis of the successful application of this material in photovoltaic applications. CH3NH3PbI3 in fact shows a good energy level alignment with respect to the many of the most popular ETM/HTM [1 2], which is a crucial prerequisite for an effective photovoltaic working mechanism.

We performed DFT simulations for the CH3NH3PbI3 perovskites/C60 interface, considering periodic slab models for the perovskite and for the coupled system. We find that the alignment of the electronic levels of the two components depends on two factors. On the one hand, the surface termination plays a fundamental role in determining the work function of the perovskite, with the surface terminating with Methylammonium and Iodide that shows a positive electronic alignment with respect to C60 (and most of the common HTM and ETM materials) and the one terminating with Iodide and Lead that shows valence and conduction bands too low in energy. On the other hand, when C60 interacts with perovskite, supramolecular interactions take place (polarization effects, electron charge transfer and state mixing), which further affect the energy level alignment. The present results not only provide a thorough comprehension of the electronic effects taking place at the CH3NH3PbI3/C60 interface but they also explain apparently contrasting experimental measurements reported in the recent literature [2-3].

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Variational exact diagonalization method for Anderson impurity models

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We describe a variational approach to solving Anderson impurity models by means of exact diagonalization. Optimized parameters of a discretized auxiliary model are obtained on the basis of the Peierls-Feynman-Bogoliubov principle. Thereby, the variational approach resolves ambiguities related with the bath discretization, which is generally necessary to make Anderson impurity models tractable by exact diagonalization. The choice of variational degrees of freedom made here allows systematic improvements of total energies over mean field decouplings like Hartree-Fock. Furthermore, our approach allows us to embed arbitrary bath discretization schemes in total energy calculations and to systematically optimize and improve on traditional routes to the discretization problem such as fitting of hybridization functions on Matsubara frequencies. Benchmarks in terms of a single orbital Anderson model demonstrate that the variational exact diagonalization method accurately reproduces free energies as well as several single- and two-particle observables obtained from an exact solution. Finally, we demonstrate the applicability of the variational exact diagonalization approach to realistic five orbital problems with the example system of Co impurities in bulk Cu and compare to continuous-time Monte Carlo calculations. The accuracy of established bath discretization schemes is assessed in the framework of the variational approach introduced here.

Tuning of optical properties by layer engineering tin chalcogenide-graphene van der Waals heterostructure

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Van der Waals (vdW) heterostructures are of significant importance in terms of tailoring of electronic and optical properties by combining different 2D materials. In this regard it may be worth studying tin dichalcogenides (SnX_2) which have promising photovoltaic properties in superlattices with other layered 2D materials. In this work we study the optical properties SnX_2 (here SnS_2 and $SnSe_2$) and Graphene (GR) vdW trilayer heterostructures. Density functional theory simulations with GGA-PBE, inclusive of DFT-D2 vdW corrections are carried out to calculate the bandstructure, density of states and optical absorption spectra. Results show that the optical absorption of the SnX_2-GR-SnX_2 heterostructures is significantly different, form the pure monolayers (1L) and trilayer (3L) of the constituent materials themselves. Each of the three individual configurations shows distinctly differing absorption spectrum, in terms of varying magnitude of absorbance and especially the absorption in the 3-4eV region. The presence of Graphene between SnX2 layers seems to enhance the absorption around ~4eV, while the very strong absorption of graphene around 1.65 eV is quenched in all the three vdW heterostructures. Introduction of Graphene also leads to the emergence of a split absorption peak around 4.65 eV in SnS_2-GR-SnS_2. The emergence of a minor hump in absorption in the range 0.4-0.8 eV, of $SnSe_2$-GR-$SnSe_2$ indicates possibility for IR absorption, and is something unseen in the 3L $SnSe_2$ or 3L Graphene individually. Such tuning of optical properties by rearrangement of layers in a vdW heterostructure offers good prospect for optoelectronic applications.

Influence of size and shape of nano-islands of hexagonal boron nitride (hBN) on optical and transport properties of hBN embedded graphene nanoribbons

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In this work we report the electronic and optical properties of graphene nanoribbons (GNR) with embedded hexagonal boron nitride (hBN) nano-islands. Armchair GNRs with hBN islands of varying shapes and sizes (such as diamond, triangle and square) were simulated with density functional tight binding (DFTB) method. Transport calculations were carried out with DFTB- non equilibrium Green’s function (NEGF) method, while optical properties were obtained with a single particle Kubo-Greenwood formula for calculating the dielectric susceptibility tensor. Simulations show that the carrier transmission properties are significantly altered, with triangular island hBN achieving many transmission states near the Fermi level, while diamond and square shaped islands showing more semiconducting transmission. In all the cases loss of staircase like transmission behavior of pure GNR is lost due to symmetry breaking. The optical absorption spectra also tends to show more distinguishable peaks compared to pure GNR. Here also the triangular hBN island seems to impact the optical spectra more than the other shapes. Such altering of electronic and optical properties by controlling the shape of the embedded hBN nano-island, can be of interest in nanoelectronics and optoelectronics.

Guidelines for organic photovoltaics from a simple kinetic model **P30**

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Despite of the great progress for the recent decade, the efficiencies of organic solar cells (OSC) are still significantly lower than those of inorganic ones. Theoretical modeling of the OSC operation can predict their ultimate efficiency and provide a roadmap for their further improvement.

In this study, we formulate an OSC model suggesting the kinetic, i.e. non-equilibrium, nature of the OSC operation. We focus on the process of charge separation according to the two-step charge generation model via intermediate hot charge-transfer (CT) states. The first step, CT state formation, is described by Marcus model [1], while the second step, CT state dissociation into free charges, is described by Onsager-Braun theory [2] modified to account for the excess energy (“hotness”) of the states. In our modeling, excess energy is responsible for increased mobility of the non-thermalized charges upon CT state dissociation, which is in accordance with the recent experimental findings [3].

Within the frames of the suggested model, we address the impacts of the optical bandgap, driving force, geminate recombination rate, charge mobility, average electron-hole separation in CT state, dielectric permittivity and reorganization energy on the organic solar cell efficiency. Our results show that the best way to increase the OSC efficiency is to use materials with low reorganization energy. The model also advises to use relatively large bandgaps (ca. 1.5-1.8 eV) as compared to that suggested by the Shockley-Quiesser model. We compare our findings with that of the previously proposed models and discuss the physical reasons underlying the obtained results.

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This work was supported by Russian Foundation of Basic Research (project # 16-32-00870)

DFT simulations on singlet fission

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We describe electronic structures for organic molecules, which are interesting for current research on organic solar cells, with density functional theory (DFT). By doing so, we present additional insight on the processes called singlet fission, which is a phenomenon that occurs in this field of work. In the process of singlet fission, a single singlet excitation is split among two molecules and dissociates into two triplet excitations. In the experiment only the singlet excitation and an additional, non radiating decay can be observed. With DFT it is possible to estimate the possibility of triplet fission on an energetic basis. Also the triplet states are feasible and characterizations of this triplet states are executed. By doing so, possibilities are given to experimentally show triplet population and proof the occurrence of singlet fission. A further project is to investigate van der Waals forces. For simple systems, the van der Waals interaction is well know and leads to a weak, attractive force. In more complex systems the van der Waals interaction can play an important role and even change its nature and become repulsive. The primary characteristics of the van der Waals potential are given by the London formula U VdW ~ C 6 / R 6 , where the C 6 coefficients are dictated by the polarisability and the electronic states of the molecule. Hereby the occupied as well as the unoccupied states are involved, due to virtual transitions. These virtual transitions also have a big influence on the sign of the C 6 coefficient. For a ground state molecule only upward transitions to higher energy levels are possible and the C 6 coefficient is always positive. For excited state molecules also downward transitions are possible, the C 6 coefficient can change its sign and the van der Waals interaction can get repulsive. Time dependent DFT (TDDFT) and Greens-function methods (GW) give access to these quantities. With this, we aim to obtain a better understanding of Van der Waals forces in general and investigate especially excited states molecules with repulsive van der Waals forces.

Real space picture of electronic correlations in 2d materials

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In this work, we investigate electronic correlations in real space in twodimensional materials. For a generic 2d semiconductor model we use the configuration interaction method to calculate electron-hole-excitations in real space and the spatial distribution of the two particle spectral function. For a monolayer in a homogeneous dielectric environment, we see that correlation effects are strongest when electron and hole are localized in the same unit cell and get weaker with longer distances. Thus, the complete cancellation of exchange and binding effects can only be found for the ground state excitations where electron and hole are close together. On top of that, we investigated the two-particle properties of a type II heterojunction, which was induced into the monolayer by a spatially structured dielectric environment (see Ref. [1]). We find, that low energy states are hardly influenced by the effect of an interface, whereas higher excitations are affected more strongly upon larger separation of electron and hole.

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Supramolecular organization of close-packed dye molecules in zeolite channels: photochemical properties

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Photoactive species can be effectively organized inside the one dimensional nanochannel system of Zeolite L (ZL), an important step in the realization of hierarchical multifunctional composite materials for a broad range of applications. Low concentrations of dye molecules per ZL unit cell are normally used in these composites and scarce attention has been devoted to very highly packed dye-ZL systems.(1) In particular, their electronic absorption and emission properties remain, to date, unexplored. By adopting an integrated experimental-modeling strategy, we realize and study high dye-loading ZL-based materials characterized by different types and content of dye molecules. In particular, we selected the Fluorenone (FL) and Thionine (Th) dyes and fabricated FL/ZL and mixed Th-FL/ZL hybrids exhibiting a high degree of packing. We determine the supramolecular organization of the closely packed chromophores inside the ZL channels and their electronic absorption, emission and energy transfer properties. X-ray diffraction, IR, thermogravimetric, Uv-vis, luminescence and energy transfer (FRET) data are discussed and rationalized in light of theoretical modeling results.

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Electronic and optical excitations at the pyridine@ZnO hybrid interface

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Insight from ab initio theory is essential in order to gain an understanding of opto-electronic properties of hybrid materials, such as the correct level alignment and the creation of hybrid excitons. We investigate a prototypical hybrid inorganic/organic system composed of a pyridine molecule, chemisorbed on a non-polar ZnO(10-10) surface, using the interface geometry as optimized by Hofmann et al. [1] as a starting point for our calculations. We employ all-electron density-functional theory in combination with many-body perturbation theory (G0W0/BSE). The G0W0 approximation describing one-particle excitations is used to determine the electronic structure, while the Bethe-Salpeter equation describing two-particle excitations is solved to obtain the absorption spectrum. We focus on the nature of optical excitations at the interface, discussing the formation of hybrid electron-hole pairs.

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Specific interlayer states coupling dependent ultrafast charge transfer in WS2/MS2 bilayers

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Despite weak interlayer interactions and strong in-plane exciton binding in van der Waals heterostructures made of two-dimensional (2D) layered materials including graphene, hexagonal boron nitride and transition-metal dichalcogenides (TMDs), small but finite quantum couplings between the layers exist which drive fantastic ultrafast phenomena. Based on state-of-the-art real-time time-dependent density functional theory, we find that the interlayer hole transfer occurs within 150 femtosecond (fs) upon photoexcitation. The process is highly sensitive to the packing structure of the heterojunction, e.g. stacking modes and vertical distances between two atomic layers. Ultrafast charge transfer from MoS2 to WS2 is observed in some stacking modes, while other stacking modes exhibit much slower charge separation with characteristic lifetime of several picoseconds. The rate of electron-hole separation in such a system can be also effectively tuned by interlayer distances. Electronic couplings between layers were found to be responsible for the distinct hole transfer time in excited states. Our work unveils the potential of 2D TMD heterostructures for quantum control of the layer degree of freedom and for optoelectronic device applications thanks to their tunable dynamic properties.

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