

CPP 3: Molecular Electronics and Excited State Properties I

Time: Monday 9:30–12:45

Location: ZEU 260

CPP 3.1 Mon 9:30 ZEU 260

A first principles study of the influence of the protein environment on electronic excitations in a bacterial reaction center — ●SABRINA KROLL, STEPHAN KÜMMEL, and LINN LEPPERT — Institute of Physics, University of Bayreuth, 95440 Bayreuth, Germany

The reaction center (RC) lies at the heart of the photosynthetic process of energy transfer, and is strongly conserved across plants, algae and bacteria. The pigment-protein complexes of most RCs are heterodimeric and charge transfer and separation occur along only one of two similar cofactor branches. The mechanism of primary charge transfer in the RC of purple bacteria has been studied in quite some detail. However, many open questions remain, regarding the relationship between the RC's structure and functionality.

Here, we use the purple bacterium *Rh. sphaeroides* as a model system for elucidating the effect of the protein environment on electronic excitations in the RC. We explicitly include four Bacteriochlorophylls (BCL), i.e. the special pair dimer and the accessory BCLs in both branches, as well as all amino acids in their vicinity in our first principles time-dependent density functional theory calculations that use an optimally tuned range-separated hybrid. We discuss the effect of systematically including larger parts of the environment on electronic structure and excitations as a first step towards entirely non-empirical calculations of charge transfer in these systems.

CPP 3.2 Mon 9:45 ZEU 260

Electronic excitations of bacteriochlorophyll with ab initio Green's function-based many-body perturbation theory — ●ZOHREH HASHEMI and LINN LEPPERT — Institute of Physics, University of Bayreuth, 95440 Bayreuth, Germany

Bacteriochlorophyll (BCL) molecules are one of the main pigments responsible for excitation energy transfer and charge separation in bacterial photosynthesis. Accurate calculation of their electronic structure and excited states from first principles, is a necessary prerequisite for simulating these processes without employing empirical parameters.

Here we present a comprehensive study of charged and neutral excitations in free-standing BCLa, as found in the Light Harvesting 2 complex of the purple bacterium *Rhodobacter sphaeroides*. We evaluate the accuracy of Green's function-based many-body perturbation theory within the GW+Bethe-Salpeter equation (BSE) approach and time-dependent density functional theory (TDDFT), and benchmark to theoretical values and experimental data. Furthermore, we discuss the importance of numerical convergence and partial self-consistency in the GW approach, and the role of the exchange-correlation functional used in our TDDFT calculations and as starting point for constructing zeroth order approximations to the one-particle Green's function G and the screened Coulomb interaction W .

CPP 3.3 Mon 10:00 ZEU 260

Untersuchung der Anregungsmechanismen organischer Materialien durch ultrakurz gepulste mid-IR Laserstrahlung — ●THEO PFLUG^{1,2}, MARKUS OLBRICH¹, PHILIPP LUNGWITZ¹ und ALEXANDER HORN¹ — ¹Laserinstitut Hochschule Mittweida, 09648 Mittweida — ²Technische Universität Chemnitz, 09126 Chemnitz

Diese Arbeit liefert erste Erkenntnisse zur Anregung von Vibrationsmoden und nachfolgende Bearbeitung organischer Materialien mittels mid-IR Laserstrahlung. Bei der Verwendung von ultrakurz gepulster Laserstrahlung kann jedoch neben der resonanten Anregung der Moleküle auch eine nichtlineare Anregung des Elektronensystems erfolgen. Ziel der Untersuchungen ist daher ein Vergleich der resultierenden Abtragsstrukturen nach nichtlinearer elektronischer Anregung und nach der Anregung der Molekülschwingungen von PMMA mittels ultrakurz gepulster mid-IR Laserstrahlung mit Pulsdauern im Femto- bis Pikosekundenbereich, sowie die Untersuchung der Dynamik der Anregung mittels Pump-Probe-Ellipsometrie. Bei Pulsdauern im Femtosekundenbereich werden Elektronen durch Tunnelionisation angeregt, wodurch ein Anstieg des Extinktionskoeffizienten k und ein Abtrag unabhängig von der Wellenlänge hervorgerufen wird. Durch Erhöhung der Pulsdauer bis zu einigen Pikosekunden verringert sich die Anzahl der durch nichtlineare elektronische Anregung erzeugten quasi-freien Ladungsträger, sodass lediglich bei der Resonanzfrequenz der C-H Schwingung bei $\lambda_{\text{pump}} = 3,4 \mu\text{m}$ Materialabtrag stattfindet und

keine Änderung des Extinktionskoeffizienten für alle Wellenlängen detektierbar ist.

CPP 3.4 Mon 10:15 ZEU 260

Quantitative Predictions of Photoelectron Spectra in Amorphous Molecular Solids from Multiscale Quasiparticle Embedding — ●GIANLUCA TIRIMBÓ^{1,4}, XANDER DE VRIES², CHRIST WEIJTENS², PETER BOBBERT^{2,4}, TOBIAS NEUMANN³, REINDER COEHOORN^{2,4}, and BJÖRN BAUMEIER^{1,4} — ¹Department of Mathematics and Computer Science, TU Eindhoven (NL) — ²Department of Applied Physics, TU Eindhoven (NL) — ³Nanomatch GmbH, Eggenstein-Leopoldshafen (DE) — ⁴Institute for Complex Molecular Systems, TU Eindhoven (NL)

We present a first-principles-based multiscale simulation framework for quantitative predictions of the high-energy part of the Ultraviolet Photoelectron Spectroscopy (UPS) spectra of amorphous molecular solids. The approach combines a deposition simulation, many-body Green's Function Theory, polarizable film-embedding, and multimode electron-vibrational coupling and provides a molecular-level view on the interactions and processes giving rise to spectral features. This insight helps bridging the current gap between experimental UPS and theoretical models as accurate analyses are hampered by the energetic disorder, surface-sensitivity of the measurement and the complexity of excitation processes. We demonstrate the capabilities of the simulation approach studying the spectrum of two isomers of archetypal materials showing a clearly separated HOMO peak in experiment. The excellent agreement suggests that our approach provides a route for determining the HOMO energy with an accuracy better than 0.1 eV.

CPP 3.5 Mon 10:30 ZEU 260

Accuracy of optimally-tuned range-separated hybrid functionals for the calculation of excited-state molecular geometries — ●BERNHARD KRETZ and DAVID ALEXANDER EGGER — Department of Physics, Technical University of Munich, Germany

An accurate description of excited-state structural dynamics of molecules is essential for the computational modeling of photochemical processes (e.g., for photocatalysis). Often, geometries optimized for the lowest-lying excited state serve as the starting point of such investigations. These geometries can be obtained either by time-dependent density functional theory (TD-DFT) or by high-level wave-function methods. Even though TD-DFT based calculations are computationally very efficient, in many cases they are less accurate compared to computationally more expensive wave-function methods[1]. However, efforts made to reduce the gap in accuracy between TD-DFT and wave-function methods recently lead to the development of the very promising class of optimally-tuned range-separated hybrid (OT-RSH) functionals[2].

In this computational study, we evaluate the precision of excited-state structures obtained with TD-DFT and OT-RSH for a selection of organic molecules. Focusing on structural parameters (e.g., bond lengths, bond angles, etc.) of the lowest-excited singlet states, we benchmark our results by comparison to high accuracy wave-function data from literature.

[1] C. Azarias, J. Phys. Chem. A, 121, 32, 6122 (2017)

[2] L. Kronik et al., J. Chem. Theory Comput., 8, 5, 1515 (2012)

CPP 3.6 Mon 10:45 ZEU 260

Photophysics of tetracene-pentacene blends — ●CLEMENS ZEISER¹, LUCA MORETTI², MARGHERITA MAIURI², GIULIO CERULLO², and KATHARINA BROCH¹ — ¹Institute for Applied Physics, University of Tübingen, Germany — ²Department of Physics, Polytechnic University of Milan, Italy

Pentacene (PEN) and tetracene (TET) are prototypical compounds for the investigation of singlet fission (SF), a process that has been extensively studied in the last decade due to its potential application in solar cells. [1] Most studies on SF examine thin films, nanoparticles, single crystals or solutions of *neat* compounds, and only few studies on doped single crystals and mixed thin films have been reported [2,3]. In this study we investigate the photophysics of mixed films of PEN and TET using transient absorption spectroscopy. We find the lowest excited singlet and triplet states in PEN:TET blends to be delocalized over both compounds and will discuss the implications for the singlet

fission dynamics in these blends.

- [1] M. Smith et al., *Chem. Rev.* 110, 6891 (2010)
 [2] N. Geacintov et al., *Chem. Phys. Lett.* 11, 504 (1971)
 [3] V. O. Kim et al., *J. Chem. Phys.*, 151, 164706 (2019)

CPP 3.7 Mon 11:00 ZEU 260

Electronic and optical properties of BCF-doped oligothiophenes from ab initio many-body theory — ●RICHARD SCHIER, ANA VALENCIA, and CATERINA COCCHI — Humboldt-Universität zu Berlin und IRIS Adlershof

Doping in organic semiconductors is an attractive research area for molecular electronics although the fundamental mechanisms ruling it are not yet fully understood. Recently, Lewis-acids such as tris(pentafluorophenyl)borane (BCF)^[1] have been regarded with particular interest as a new class of dopants for organic semiconductors^[2]. To gain insight into the microscopic properties of these materials, we investigate the electronic structure and optical properties of donor/acceptor interfaces formed by a single quarterthiophene (4T) molecule doped by a BCF species. For comparison, we consider also other adducts with 4T doped by hexafluorobenzene (C₆F₆) and the trihalide BF₃. We carry out our study from first principles, in the framework of hybrid density-functional theory and many-body perturbation theory. For all systems, we find that the frontier orbitals are poorly hybridized and rather segregated on the donor or the acceptor depending on the specific level alignment of the system. As a consequence, the optical spectra of the systems appear almost as a superposition of those of the respective constituents. A careful analysis reveals interaction signatures in the form of dark excitations and peak shifts^[3].

- [1] Körte et al., *Angew. Chem.* 56, 8578 (2017) [2] Yurash et al., *Nat. Mater.* 18, 1327 (2019) [3] Schier et al., to be submitted (2020)

15 min. break

CPP 3.8 Mon 11:30 ZEU 260

Ab initio modelling of local interfaces in doped organic semiconductors — ANA MARIA VALENCIA, ●GUERRINI MICHELE, and CATERINA COCCHI — Humboldt-Universität zu Berlin

Despite the intensive efforts in the last decade, a clear and comprehensive understanding of the microscopic properties of doped organic semiconductors is still missing. Due to the complexity of these systems, which notoriously exhibit high level of disorder, also the results from quantum-mechanical ab initio methods are somehow constrained by the choice of the model structures. For a reliable prediction of electronic and optical properties, it is essential to rationalize the role of local interfaces between interacting donor and acceptor species. We address this problem from hybrid density-functional theory and many-body perturbation theory, investigating the structural, electronic, and optical properties of oligothiophenes doped by F4TCNQ. We consider different structures from isolated dimers and trimers, to periodic stacks and crystalline arrangements. Our results show that, depending on the amount and the nature of the local donor/acceptor interfaces, the choice of the simulated structure critically impacts the resulting electronic structure and degree of charge transfer. On the other hand, the optical spectra appear less sensitive to these characteristics, although a detailed inspection of the electron and hole densities discloses different excitation character depending on the relative donor/acceptor concentration [1] as well as on the donor length [2].

- [1] Valencia, Guerrini, Cocchi, submitted (2019).
 [2] Valencia & Cocchi, *JPC* 123, 9617 (2019).

CPP 3.9 Mon 11:45 ZEU 260

Excited State Dynamics of Tetracene-Acceptor Blends — ●CHRISTOPH THEURER¹, JULIAN HAUSCH¹, CLEMENS ZEISER¹, VIPILAN SIVANESAN², PETRA TEGEDER², and KATHARINA BROCH¹ — ¹Eberhard Karls Universität Tübingen, Institut für Angewandte Physik, Tübingen — ²Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut, Heidelberg

Charge transfer between electron donating and accepting organic semiconductors (OSCs) is pivotal for exploiting the full potential of OSCs in devices [1].

Tetracene is a prototypical OSC and exhibits interesting optical properties and effects like singlet fission, making it a promising material for solar energy conversion [2]. The competition between charge transfer to organic acceptors and singlet fission has, however, received

little attention in tetracene so far [3][4]. In this work, blends of tetracene and two common, strong acceptors, F6-TCNNQ and F4-TCNQ, have been grown and investigated. Based on thorough structural and morphological investigations we studied and compared the photophysics of blends with different mixing ratios. The dynamics of these fundamentally interesting systems were examined by transient absorption spectroscopy.

- [1] Forrest, S. R., *Nature* 428 (2004) [2] Smith, M. B., and Michl, J., *Chemical Reviews* 110 (2010) [3] Hu, P., et al., *CrystEngComm* 19 (2017) [4] Yost, S., et al., *Nature Chem* 6 (2014)

CPP 3.10 Mon 12:00 ZEU 260

Morphological Tuning of the Dual Luminescence in Zinc-Phthalocyanine OLEDs — SEBASTIAN HAMMER¹, ●THOMAS FERSCHKE¹, GABRIEL VON EYB¹, and JENS PFLAUM^{1,2} — ¹Experimental Physics VI, Julius Maximilian University, 97074 Würzburg — ²ZAE Bayern, 97074 Würzburg

In the field of telecommunications, a rising demand for opto-electronic devices operating in the near infrared can be identified. Moreover, in order to enhance the transmission capabilities of such future photonic devices, versatile, multi-emissive materials are required.

For this purpose, we investigate the first order α -to- β phase transition and its influence on the optical properties of crystalline Zinc-Phthalocyanine (ZnPc) thin films. Under optical excitation two distinct intensity maxima are observed at 780 nm and 930 nm. The emission component around 930 nm can be assigned to excimer emission of the ZnPc α -phase [1], whereas luminescence at 780 nm originates from bulk Frenkel excitons of the corresponding β -phase. Comprehensive temperature and time dependent studies on the phase transition show the feasibility of a controllable luminescence shift of the layers. The phase transfer kinetics can be modelled by a Johnson-Mehl-Kolmogorov-Avrami model based on growth of polyhedral grains [2]. Utilizing these findings, we demonstrate the implementation of dual luminescent OLED devices based on a single ZnPc emissive layer with balanced near infrared emission.

- [1] V. Kolb and J. Pflaum, *Opt. Express* 25, 6678 (2017)
 [2] M. Avrami, *J. Chem. Phys.* 8, 212 (1940)

CPP 3.11 Mon 12:15 ZEU 260

Substituent approach in molecular design of phosphorous compounds for OLED emitters — ●JONAS KÖHLING, GERD-VOLKER RÖSCHENTHALER, and VEIT WAGNER — Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Organic light emitting diodes (OLEDs) are one of the leading technologies used for display fabrication. Currently, the main challenge in OLED technology is to synthesize and design efficient and stable emitters. To achieve this goal, it is of great interest to evaluate and optimize molecular design of a large number of possible organic molecules prior to their synthesis. In this study, we have used a substituent approach to design and analyze a large number of derivatives of phosphorous compound. The core molecule is chosen so that it meets requirements of the third generation of the OLED emitters and allows for the thermally activated delayed fluorescence. The core molecule is systematically varied by introduction of substituents from strong electron withdrawing groups (EWG) towards strong electron donating groups (EDG). By using density functional theory (B3LYP/6-31+G(d,p)) calculations, we show that EDG substituents are able to tune the bandgap of the potential OLED emitters. On the other hand, EWG substituent groups can be used to tune the band alignment of the core molecule.

CPP 3.12 Mon 12:30 ZEU 260

Characterization and control of aggregation in doped poly(3-hexylthiophene-2,5-diyl) solutions — ●AHMED E. MANSOUR^{1,2}, DOMINIQUE LUNGWITZ¹, THORSTEN SCHULTZ^{1,2}, MALAVIKA ARVIND³, ANA M. VALENCIA¹, CATERINA COCCHI¹, ANDREAS OPITZ¹, DIETER NEHER³, and NORBERT KOCH^{1,2} — ¹Institut für Physik & IRIS Adlershof, Humboldt Universität zu Berlin, Germany — ²Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Germany — ³Institut für Physik und Astronomie, Universität Potsdam, Germany

Chemical doping of poly(3-hexylthiophene-2,5-diyl) (P3HT) is commonly achieved by mixing solutions of the dopant molecules and the polymer in predetermined volumes based on the desired dopant ratio. Aggregation in doped P3HT is typically observed as a result of the solution-mixing process, due to decreased solubility of the mixture. In this work, we provide means for characterizing the presence of doped aggregates and their relative amounts with respect to doped isolated

polymer chains in tris(pentafluorophenyl)borane (BCF) doped P3HT solutions. This is achieved by the distinction of signatures in the optical absorption spectrum due to polarons in doped aggregates on the one hand, and doped isolated chains on the other hand. We further rely on these signatures to investigate the influence of dopant ratio and

absolute concentration of the solution mixture on the relative amount and the size of the aggregates. Finally, we quantify the degree of doping as a function of the structural form, showing a larger degree of doping in the aggregates as compared to the isolated chains.