

CPP 96: Organic Electronics and Photovoltaics IV

Time: Thursday 15:00–18:00

Location: ZEU 260

CPP 96.1 Thu 15:00 ZEU 260

Single particle spectral functions of the Holstein model for organic crystals — ●MICHEL PANHANS and FRANK ORTMANN — Center for Advancing Electronics Dresden, Technische Universität Dresden, 01069 Dresden

Despite multifaceted theoretical efforts to understand the effect of electron-phonon interaction on electrons and holes in organic semiconductors, there is no unbiased approach to justify or falsify typical approximations in the existing theories. One of the central questions is under which conditions a classical or a quantum treatment of the vibrations is appropriate. We present a numerical method to study the role of electron-phonon coupling in the Holstein model for single-particle spectral functions of polarons. We compare the spectral functions of an exact treatment of electron-phonon coupling with the static approximation where the modes are decoupled. We find parameter regions where such a treatment of the modes is or is not justified. We therefore are able to separate modes that may be treated quasi-classically or quantum mechanically. The results can be used to predict single-particle spectral functions for organic model crystals such as rubrene.

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Strongly anisotropic charge transport in crystalline polymer-based materials — ●PETROS SKOPELITIS, MICHEL PANHANS, SEBASTIAN HUTSCH, THORSTEN ARNOLD, and FRANK ORTMANN — Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden

The description of charge transport in polymer materials is complicated by the effect of electron-phonon coupling, electronic anisotropy and uncertain transport mechanism. Here we focus on the relation between intrachain and interchain transport of polymer materials and study crystalline PBTTT-C14 as a model system. We derived an expression for the Kubo formalism that combines coherent and incoherent transport in different directions. The validity of the traditional hopping formula for the mobility is studied and compared to the formula we derived from the Kubo formalism. Various intrinsic aspects of the PBTTT-C14 system are studied and analysed, such as phase coherence, diffusivity and mobility edges. The insights we acquired from the analysis made it possible for us to calculate, within the assumptions of our framework, the transfer integrals in the direction of the alkyl chains in PBTTT-C14, using experimental measurements for conductivity and mobile carrier density as input.

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Why is electronic transport in conjugated organic materials rather inefficient? From organic semiconductors to covalent organic frameworks. — ●CHRISTIAN WINKLER, OLIVER T. HOFMANN, and EGBERT ZOJER — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz

In a recent work [1] we demonstrated for organic semiconductors using dispersion-corrected density-functional theory that molecular arrangements with high inter-molecular electronic couplings are typically energetically unfavorable, which can be traced back to Pauli exchange repulsion of neighboring π -systems. This correlation is not only of importance for charge transport in organic semiconductors but also plays a crucial role in electrically conductive covalent organic frameworks (COFs). COFs are crystalline structures, where the molecular building blocks are covalently bonded within a 2D plane and these planes are then π -stacked. We will show that also in these systems, Pauli exchange repulsion prevents a perfectly coplanar stacking of consecutive layers. Instead, one has to expect small shifts between consecutive layers, where these shifts have only a very minor impact on the powder x-ray diffractograms of the studied COFs. In spite of this small impact on structural parameters, the slip can change the electronic coupling between consecutive COF sheets by orders of magnitude. This suggests that for optimizing charge transport in organic materials, one cannot rely on the (self) assembly of the π -systems but needs to include additional chemical functionalities that modify the packing motif. [1] C. Winkler et al., Chem. Mater. 2019, 31, 17, 7054-7069

CPP 96.4 Thu 15:45 ZEU 260

Explaining Charge Mobility Regimes in Amorphous Materials: The correction energy concept — MARKUS KRAMMER¹, CHRIS GROVES², and ●KARIN ZOJER¹ — ¹Institute of Solid State

Physics, NAWI Graz, Graz University of Technology, Austria — ²Department of Engineering, Durham University, United Kingdom

Charge transport in amorphous materials like organic semiconductors happens via hopping between localized states of profound energetic disorder. The charge mobility reflects how swiftly charges are transported through such an energy landscape. Evidently, it is desirable to predict mobility-limiting bottlenecks and roadblocks directly from analyzing the energy landscape. However, external electric fields and interactions with other charges are as relevant for transport as the landscape, so that mobility-limiting features can be quantified only after having fully simulated entire charge trajectories respecting those influences. We developed a new simulation technique to calculate the mobility, which further permits to predict and interpret the dependence of the mobility on the external electric field and the charge density based on the energy landscape. The key idea is to modify the energy landscape by local correction energies that account for the ability of the charges to explore the underlying local landscape in the presence of all other charges, external electric fields, and temperature. To demonstrate the appealing ease of interpreting our simulations, we will explain the reasons for the field and the charge carrier-density dependence of the mobility.

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Ordered phases of (A1-D-A2)_n polymers: What can we learn from simulations? — DEYAN RAYCHEV^{1,2}, GOTTHARD SEIFERT^{2,3}, JENS-UWE SOMMER^{1,2,4}, and ●OLGA GUSKOVA^{1,2} — ¹IPF Dresden — ²DCMS, TU Dresden — ³Theoretische Chemie, TU Dresden — ⁴Institut für Theoretische Physik, TU Dresden

The lamellar morphologies of (A1-D-A2)_n polymers consisting of dike-topyrrolopyrrole (A1 with linear or branched alkyls) and benzothiadiazole (A2) acceptor units linked together via aromatic donor (D, thiophene or furan) are studied using a combination of DFT and MD simulations [1]. We show that the morphology of the macromolecular arrays is very sensitive to the branching of the alkyl substituents of DPP cores and to D type. They affect not only the planarity of the conjugated macromolecules but also cause various π - π stacking distances and lamellar intervals in the ordered phases of polymers. The next results are related to the stacking motifs of the conjugated copolymers. We conclude that the samples with linear side chains have segregated stacking motif, in which acceptor units and donors build their own columns. On the contrary, branched alkyls lead often to defective structures and irregular stacking.

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[1] D. Raychev, et al. Macromolecules, 2019, 52 (3) 904.

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Predicting the reorganization energies of organic semiconductors via machine learning — ●KE CHEN, CHRISTIAN KUNKEL, JOHANNES MARGRAF, and KARSTEN REUTER — Technical University of Munich, Garching, Germany

The chemical space of possible organic semiconductors is enormous, and only few of them have been experimentally tested so far. It is therefore likely that many high performance organic semiconductors are still unknown. High-throughput computational screening can help accelerate their discovery, in particular when combined with highly efficient machine learning (ML) models. In this contribution, we focus on the so-called reorganization energy, which is one of the most critical molecular properties correlated with high charge carriers mobility in organic semiconductors.

The ML models presented herein use the smooth overlap of atomic positions (SOAP) for a local representation of atomic environments [1]. Based on this, two different global representations are studied to represent the molecular structures, namely the average global kernel and the 'auto-bag' method of Hammer et al. [2]. These representations are combined with linear and kernel ridge regression.

We find that these ML models can reliably identify the best candidates in a large chemical space of organic molecules. Furthermore, data-efficiency, prediction cost and the reliability of uncertainty estimates are compared.

[1] A. P. Bartók et al., Phys. Rev. B 87, 184115 (2013). [2] S. A. Meldgaard et al., J. Chem. Phys. 149, 134104 (2018).

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Assessing Crystal Structure Prediction Based on Density Functional Tight Binding and Evolutionary Algorithms — ●SEBASTIAN HUTSCH and FRANK ORTMANN — Center for Advancing Electronics Dresden, Technische Universität Dresden, Germany

The prediction of crystal structures for organic molecules is a computationally expensive task due to the large number of atoms in the unit cell and the associated number of possible configurations. The computational load can be compensated by the use of classical force fields, which however lack transferability to new molecules and necessitate an extensive training for complex molecules. Here, we study an approach to crystal structure prediction based on evolutionary algorithms and a combination of Density Functional Tight Binding (DFTB) and Density Functional Theory (DFT). This combination allows us to cost efficiently compute crystal structures for new materials on a high level of accuracy. A comparison of the calculated crystal structures with experimentally known structures will be made.

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Accurate Phonon Calculations in Molecular Crystals: The Instructive Case of Naphthalene — ●TOMAS KAMENCEK^{1,2}, SANDRO WIESER¹, NATALIA BEDOYA-MARTÍNEZ³, JOHANNES P. DÜRHOFT⁴, ROCHUS SCHMID⁴, and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, Graz University of Technology, Austria — ²Institute of Physical and Theoretical Chemistry, Graz University of Technology, Austria — ³Materials Center Leoben, Austria — ⁴Chair of Inorganic Chemistry 2, Ruhr University Bochum, Germany

Over the past decades the properties of molecular crystals have been studied extensively to improve the performance of organic electronic devices. Many of the materials properties relevant in this context are crucially affected by phonons. For example, strong electron-phonon coupling is a limiting factor for charge transport in molecular crystals, and entropic contributions from phonons play a decisive role for the relative stability of polymorphs. The simulation of phonon band structures with ab initio methods like dispersion-corrected density-functional theory, however, poses a sizable challenge for all but the simplest systems. Therefore, here we test the suitability of more approximate methods, which can be applied not only to simple systems, but also to practically relevant materials. These methods comprise density-functional tight binding and various classical force fields (FFs). Besides transferable FFs of varying sophistication (GAFF and COMPASS) we tested MOF-FF which was specifically parametrized for our benchmark system. As the latter we chose deuterated naphthalene, for which phonon band structures have also been studied experimentally.

15 min. break

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Numerical Modeling of Transient Electroluminescence based on Thermally Activated Delayed Fluorescence — ●JEANNINE GRÜNE, NIKOLAI BUNZMANN, SEBASTIAN WEISSENSEEL, VLADIMIR DYAKONOV, and ANDREAS SPERLICH — Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg

Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) show increased efficiencies due to effective upconversion from the non-emissive triplet states to the emissive singlet state via reverse intersystem crossing (RISC). A promising approach in this field are donor:acceptor configurations, whereby an intermolecular exciton is formed at

the interface of two molecules, also called exciplex. A proven material combination is among others 4,4',4''-Tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA), as donor and Tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), as acceptor. The characteristic behaviour especially in transient measurements differs from what is commonly observed in state of the art intramolecular emitters. In order to gain insight into the ongoing processes in exciplex based OLEDs, we performed numerical fits on transient electroluminescence (trEL) measurements at different temperatures. The kinetic model adapted for EL measurements on TADF systems includes second order terms to consider the existing annihilation processes such as triplet-triplet annihilation. Using this procedure, we can quantify the impact of efficiency-enhancing and efficiency-reducing processes as well as the time-dependent excited state populations.

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Theoretical study of ferroelectricity in tetramethylbenzidine-tetracyanoquinodimethane (TMB-TCNQ) — ●SHOJI ISHIBASHI, SACHIO HORIUCHI, and KIYOYUKI TERAKURA — National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

Some of mixed-stack organic charge transfer complexes show ferroelectricity. Tetrathiafulvalene-*p*-chloranil (TTF-CA) is a typical example. Kobayashi et al. successfully obtained a polarization value of $6.3 \mu\text{C cm}^{-2}$ in TTF-CA [1]. This value is more than 20 times larger than that of the point charge model and their directions are opposite. We made theoretical analyses of this exotic ferroelectricity in TTF-CA in terms of Born effective charges as well as maximally-localized Wannier orbitals [2,3]. We have shown that only 2 bands below the band gap are responsible for the emergence of polarization and also that the electron flow from cell to cell on these electronic states is the origin of the exotic polarization in TTF-CA. Recently, Mezzadri et al. have reported the mixed-stack crystal structure of the low-temperature phase of tetramethylbenzidine-tetracyanoquinodimethane (TMB-TCNQ) and pointed out that this phase is potentially ferroelectric [4]. In the present study, we have applied the above-mentioned theoretical methods to investigate the ferroelectricity in TMB-TCNQ and report similarities and dissimilarities to that of TTF-CA.

[1] K. Kobayashi et al., Phys. Rev. Lett. **108**, 237601 (2012). [2] S. Ishibashi and K. Terakura, J. Phys. Soc. Jpn. **83**, 073702 (2014). [3] K. Terakura and S. Ishibashi, Phys. Rev. B **91**, 195120 (2015). [4] F. Mezzadri et al., Cryst. Growth Des. **18**, 5592 (2018).

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Theoretical Characterization and Design of Organic Open-Shell Materials: From Bi- to Tetraradicals — ●SEBASTIAN SCHELLHAMMER and FRANK ORTMANN — Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden

In recent years, organic molecules with stable open-shell ground states have attracted growing interest due to their outstanding properties, i.e. responsive spin structures, singlet fission or non-linear optical properties. Although the number of interesting material classes is growing, the molecules often have low thermal stability, hindering their use in electronic devices.

In this presentation, we will highlight routes but also dead ends in the quest for high-spin configurations in hydrocarbons. By using a computational approach based on density functional theory (DFT) and CASSCF, different structure-property relationships are discussed. We demonstrate that optimization of material properties can be achieved by manipulating the wavefunctions of the unpaired electrons. Here, well known chemical functionalization strategies such as benzannulation, push-pull design, or tuning of intramolecular interactions can be combined to create molecules with well-defined properties.