CPP 27: Molecular Electronics and Excited State Properties II

Time: Wednesday 11:30–13:00 Location: H38

CPP 27.1 Wed 11:30 H38

Break-junctions beyond single-molecule conductance — •Joseph Hamill — Department of Chemistry and Nanoscience Center, University of Copenhagen, Denmark

The challenge in nanosciences is to reliably manipulate and probe objects on the atomic and molecular scale. Single-molecule break junctions cleverly integrate a single molecule into an electric circuit, enabling measurement of its thermal, electrochemical, and electrical properties. These studies explore candidates for waste heat capture, quantum information technologies, sensors, nanomedicine, and other novel materials applications. Over the past 20 years, single-molecule break junction methods have advanced to measure current, resistance, rectification, and thermopower. Despite this progress, they are not yet a staple in every chemist's toolbox like NMR spectroscopy. Recent studies using these junctions to monitor and induce chemical reactions may change this. I will present two recent studies demonstrating their sensitivity to changes in bonding chemistry and the tautomer state of single molecules in the junction. This sensitivity is unlocked through frequency domain spectroscopy using flicker noise analysis[1] and improved machine learning approaches, such as principal component analysis and k-means clustering.[2]

[1] U. Rashid, W. Bro-Jørgensen, K. Harilal, P. Sreelakshmi, R. R. Mondal, V. Chittari Pisharam, K. N. Parida, K. Geetharani, J. M. Hamill, and V. Kaliginedi. JACS, 146, 9063-9073. [2] P. Sreelakshmi, R. Mahashaya, S. Leitherer, U. Rashid, J. M. Hamill, M. Nair, P. Rajamalli, and V. Kaliginedi. JACS, 10.1021/jacs.4c12423.

CPP 27.2 Wed 11:45 H38

Charge transport in organic semiconductors with a mapping approach to surface hopping — •Johan Runeson[1], Thomas Drayton[2], and David Manolopoulos[2] — [1]Institute of Physics, University of Freiburg, Germany — [2]Physical and Theoretical Chemistry Laboratory, University of Oxford, UK

Coupled charge-phonon systems are challenging to simulate in the intermediate regime between traditional delocalized band theory and localized polaron theory. In particular, it remains unclear which methods are suitable to describe organic semiconductors. Conventional trajectory-based methods, such as Ehrenfest dynamics and surface hopping, do not capture the correct equilibrium of mixed quantum-classical systems. In this talk, I will present a simple solution to this problem. Based on a recently developed "mapping approach to surface hopping" [1,2], we propagate trajectories on the adiabatic state with the highest population, which in contrast to previous methods is consistent with the correct quantum-classical equilibrium. We applied this methodology to charge diffusion in crystalline rubrene [3] and obtained a well-defined diffusion constant, without having to introduce the phenomenological relaxation time approximation (RTA). Our results give 30-60 % higher charge mobilities than conventional RTA calculations and shed light on experiments of the optical conductivity.

[1] J. R. Mannouch and J. O. Richardson, J. Chem. Phys. 158, 104111 (2023). [2] J. E. Runeson and D. E. Manolopoulos, J. Chem. Phys. 159, 094115 (2023). [3] J. E. Runeson, T. J. G. Drayton, and D. E. Manolopoulos, J. Chem. Phys. 161, 144102 (2024).

CPP 27.3 Wed 12:00 H38

Influence of Classical Molecular Motion on Energy Transport in Molecular Aggregates — •Ritesh Pant[1], Sebastian Wüster[2], and Alexander Eisfeld[1] — [1]Max Planck Institute for the Physics of Complex Systems, Dresden, Germany — [2]Indian Institute of Science Education and Research, Bhopal, India

Molecular aggregates can transport electronic excitation energy over large distances due to dipole-dipole interactions [1]. We explore the impact of classical thermal motion of entire monomers on this transport, considering a chain of molecules [2]. Such motion induces changes in the aggregate's geometry, thereby altering the exciton states and enabling, in certain regimes, the adiabatic transport of excitation energy. We find that, in the absence of intramolecular vibrations, the interplay between molecular motion and exciton dynamics induces oscillatory behavior in site populations, which are coupled to the motion. These oscillations occur specifically when the molecular motion is slow enough to be considered adiabatic with respect to the exciton dynamics, and their characteristics depend on the chain length, with shorter chains exhibiting more pronounced effects. We also explore the effect of intramolecular vibrations on this oscillatory behavior and investigate the conditions under which the oscillations persist or are suppressed.

[1] T. Brixner et. al., Adv. Energy Mater. 7, 1700236 (2017).
[2] R. Pant et. al., Phys. Chem. Chem. Phys. 22, 21169 (2020).

CPP 27.4 Wed 12:15 H38

Enhancing excitonic properties in organic semiconductors by aqueous ions — •Filip Podjaski — Department of Chemistry and Centre for Processable Electronics, Imperial College London, UK

While organics semiconductors (OSC) promise tailorable structure-function relationships for enhanced solar energy conversion abilities, advancement is often hindered by limiting knowledge of interwoven photo-physical processes and properties that lead to recombination losses on ultrafast time scales.[1] Herein, I discuss possibilities to measure and modify functionalized OSC' exciton behaviour, to address their recombination. For photocatalysis, interactions with aqueous ions, which are also relevant for enabling sea water use, are typically disregarded. Our time-resolved optical spectroscopy study on suspended polymer nanoparticles in presence of different salts shows how they can improve stabilization of excitons. We further introduce Terahertz permittivity measurements as convenient tool to probe the complex permittivity / dielectric properties of OSCs on ps-time scales. The permittivity defines exciton binding energy and is hence relevant for charge carrier photogeneration and transport. But its highly frequency dependent values are commonly extracted orders magnitude off the ps-regime. Our study focussing on carbon nitrides now reveals dielectric screening and transport properties at the early time scales of solar energy conversion process chains, and illustrates environmental enhancements enabled by ions.[2]

References: [1] Nat. Rev. Mater. 6, 168-190 (2021). [2] R. Jahangir, F. Podjaski et al., submitted, arxiv.org/abs/2411.06226

CPP 27.5 Wed 12:30 H38

Computational insights into open-shell molecules for applications in molecular electronics — •Susanne Leitherer[1] and Gemma C. Solomon[1,2] — [1]Department of Chemistry and Center of Nanoscience, University of Copenhagen, Denmark — [2]Niels Bohr Institute, University of Copenhagen, Denmark

Recent studies have explored a range of molecules with unpaired electrons, represented by their spin. These investigations focused on the charge transport characteristics of the molecules when interfaced with electrodes, as well as their structural rearrangements in electric fields and interactions with surfaces. The theoretical analysis of these systems frequently employs spin-polarized or symmetry-broken unrestricted density functional theory (DFT). This method has proven effective in modeling oxidized molecules exhibiting highly conductive low-energy states, characterized as 1D topological insulators[1]. However, it is well known that DFT can pose challenges for open-shell structures due to their multiconfigurational nature. We demonstrate how for a selection of polycyclic aromatic hydrocarbons - previously investigated in recent scanning probe experiments[2] - the ground state can be accurately determined using a multi-configurational short-range DFT approach[3]. [1] High Molecular Conductance and Inverted Conductance Decay over 3nm in Aminium-Terminated Carbon-Bridged Oligophenylene-Vinylenes, Krieger et al, JACS (2024); [2] Atomically resolved single-molecule triplet quenching, Peng et al., Science 373 (2021); [3] Multiconfigurational sr-DFT for open-shell systems, Hedegard et al, J. Chem. Phys. 148, 214103 (2018)

CPP 27.6 Wed 12:45 H38

Exceptionally High Two-Photon Absorption Cross Sections in Quinoidal Diazaacene-Bithiophene Derivatives — •Gabriel Sauter[1], Antonia Papapostolou[2], Audrey Pollien[1], Kathleen Fuchs[3], Kerstin Brödner[3], Jan Freudenberg[3], Uwe H. F. Bunz[3], Andreas Dreuw[2], and Petra Tegeder[1] — [1]Physikalisch-Chemisches Institut — [2]Interdisziplinäres Zentrum für Wissenschaftliches Rechnen — [3]Organisch-Chemisches Institut, Universität Heidelberg

In nonlinear optics, materials with high two-photon absorption (2PA) cross sections are crucial for bioimaging, photodynamic therapy, and 3D nanoprinting [1]. Our study highlights quinoidal diazaacene-bithiophene derivatives with exceptional 2PA cross sections, reaching 53,600 GM (850-950 nm) and 4,100 GM (1400-1600 nm), unmatched by organic chromophores of this size [3].

Using experimental z-scan techniques and TDDFT calculations, we attribute these properties to the chromophores acceptor-π-donor-π-acceptor structure, which ensures high oscillator strength and strong state coupling. These features optimize transition dipole moment alignment, maximizing 2PA efficiency.

These findings advance the development of efficient NIR-2PA materials for photonic and biomedical applications.

References:

1. F. Kröger et al., *RSC Appl. Polym.* **2024**, 2, 847.
2. K. Fuchs et al., *Angew. Chem. Int. Ed.* **2024**.