CPP 16 Electronic Structure and Spectroscopy II

Time: Wednesday 14:00–17:30 Room: ZEU 160

CPP 16.1 Wed 14:00 ZEU 160

Statistics of low energy weakly localized Frenkel exciton levels in one-dimensional disordered systems — •Mariusz Bednarz — Abteilung Theoretische Physik, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany

A novel approach to probe the statistics of low energy levels of weakly localized Frenkel states in one-dimensional disordered systems will be shown. We analyze theoretically the spectral dynamics of excitons caused by the vibration-assisted hopping over localized states. The Pauli master equation is used as a tool to describe exciton hopping. Exciton fluorescence under very narrow spectral excitation conditions, resonant with the absorption band, is put forward to uncover the regularities of the exciton spectral dynamics. Under such conditions the fluorescence spectra are composed of a narrow peak at the excitation energy and a red shifted wing. This spectral structure has a simple explanation within the framework of the band-edge local level structure which has been proven to exist in the low-energy tail of the density of exciton states. The narrow peak results from the localized exciton states (mostly with large oscillator strength) created by the pump, while the wing is formed due to possible hopping of initially created excitons to the lower energy localized states, occurring within the same localization segment as well as between different ones. We show in a very detailed manner how the statistics of low energy levels can be extracted form the wing of such spectra at zero Kelvin. The effect of the localization due to spatial correlation of molecular energetic disorder on the energy level statistic also will be shown.

CPP 16.2 Wed 14:15 ZEU 160

Double-Pole Approximation in Time-Dependent Density Functional Theory — •H. Appel[1], E.K.U. Gross[1], and K. Burke[2] — [1]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany. — [2]Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Rd, Piscataway, NJ 08854.

A simple approximate solution of the TDDFT response equations is the single pole approximation (SPA). By relating the poles of the Kohn-Sham (KS) response function to the poles of the true interacting response function, SPA provides additive shifts that correct the KS excitation energies towards the true excitations of the system. In the present work [1] we have extended the SPA to the case of two strongly coupled poles. The analysis provides a variety of new results beyond those of SPA. Most importantly, one can determine the regimes where SPA fails and provide corrections in that case. In addition corrections to oscillator strengths become accessible by using the double-pole approximation (DPA). Within the DPA we show that in certain regimes the coupling between poles can cause a transition to vanish entirely from the optical spectrum. DPA has recently been successfully applied to core-hole interaction in the X-ray absorption spectroscopy of 3d transition metals [2].

[1] Double-Pole Approximation in Time-Dependent Density Functional Theory, H. Appel, E.K.U. Gross, K. Burke, cond-mat/0510396

[2] Measuring the kernel of time-dependent density functional theory with X-ray absorption spectroscopy of 3d transition metals, A. Scherz, E.K.U. Gross, H. Appel, C. Sorg, K. Baberschke, H. Wende, and K. Burke, Phys. Rev. Lett., in print.

CPP 16.3 Wed 14:30 ZEU 160

ESR-Imaging including Conduction Electron Drift Velocity Measurement — •Malte Drescher[1], Noam Kaplan[2], and Elmar Dormann[1] — [1]Physikalisches Institut, Universität Karlsruhe(TH), D-76128 Karlsruhe, Germany — [2]Racah Institute of Physics, Hebrew University, Jerusalem, Israel

This contribution presents the results on ESR-imaging via temperature dependent pulsed X-band ESR focussing on quasi one-dimensional organic conductors, where due to their long T_2-time constants even pulsed conduction electron spin resonance and a resolution better than $10\mu m$ is possible. Additionally to depicting spin densities we succeeded in spatially resolved determining dynamic properties, e.g. spin-spin-, spin-lattice-relaxation, spin diffusion coefficient or phase transition temperatures.

Since flow measurement is an established tool in NMR-imaging, the possibility of performing ESR experiments on conduction electrons allows in principle to determine the electron spin drift velocity for given electrical current. An appropriate pulsed gradient and current ESR detection scheme was developed and the first successful experiment of detecting the phase shift in the ESR-signal induced by an applied electrical current was performed. The ohmic correlation is demonstrated in a range of more than +/- 250mA in crystals exhibiting a cross-sectional area of less than $1mm^2$ and a maximum drift velocity of 0.3 $\frac{m}{s}$ was found in the metallic phase of a radical cation salt.

CPP 16.4 Wed 14:45 ZEU 160

Multiexciton Vibrational States in α-Helical Polypeptides — •Dmitry Tsivlin and Volkhard May — Institut für Physik, Humboldt Universität zu Berlin, Newtonstr. 15, D-12489 Berlin

Studies of amide vibrations in α-helical polypeptides attracted much interest due to the mechanism of self-trapping of vibrational excitation, originally proposed by Davydov. Recently, it became possible to observe the self-trapped states in α-helices by using femtosecond infrared pump-probe spectroscopy [1].

Since for the amide vibrational states the so-called nonadiabatic limit is reached [2], theoretical description of the system requires a quantum treatment of the high-frequency amide mode coordinates as well as the coordinates of the polypeptide lattice. In the present work, by employing a multiexciton expansion of the model Hamiltonian an accurate quantum-dynamical description of vibrational states formed by amide C=O and N-H stretching modes of α-helix is presented [3]. Using the multiconfiguration time-dependent Hartree method, linear and pump-probe infrared absorption spectra are calculated by numerical time-propagation of the exciton-chain vibrational wavefunction. Formation of self-trapped exciton states is discussed within the adiabatic exciton approximation and within the full quantum approach. Interpretation of the infrared pump-probe experiments for α-helical polypeptides and for peptide model crystals is proposed [1,2].

[1] J. Edler et al., Phys. Rev. Lett. **93**, 106405 (2004)

[2] D.V. Tsivlin, V. May, and H.-D. Meyer, J. Chem. Phys., submitted

[3] D.V. Tsivlin and V. May, Chem. Phys. Lett. **408**, 360 (2004)

CPP 16.5 Wed 15:45 ZEU 160

The electronic structure of liquids studied by resonant X-ray emission (RXES) and X-ray absorption spectroscopy (XAS) in the soft X-ray range — •Oliver Fuchs[1], L. Weinhardt[1], F. Maier[1], E. Umbach[1], M. Bär[2], T. Hofmann[2], J. White[2], V. Marepally[2], C. Heske[2], M. Zharnikov[3], M. Grunze[3], and J.D. Denlinger[4] — [1]Exp. Physik II, Uni Würzburg — [2]Dept. of Chem., Univ. of Nevada, Las Vegas — [3]Angew. Physikal. Chemie, Uni Heidelberg — [4]ALS, Berkeley

The investigation of liquids by means of soft x-ray techniques is a technically challenging task since it requires a third-generation synchrotron source combined with a high-efficiency grating spectrometer, and a wet cell with an ultra-thin window separating the liquid from ultra-high vacuum. With our flow-through wet cell we have investigated the electronic structure of various liquids including H_2O, D_2O, NaOH, NaOD, ethanol, acetic acid, and various aqueous solutions. The spectra reveal details on the hydrogen bonding network of water and its temperature dependence. The investigation of aqueous solutions reveals on the one hand the effect of the solutes on the hydrogen bonds of water, and on the other hand the influence of the hydration shell on the electronic structure of the solutes. Moreover, molecular dynamics within the time scale of the core hole lifetime (a few femtoseconds) leads to isotope effects in both, RXES and XAS spectra, and can be described by theoretical molecular dynamics simulations.

CPP 16.6 Wed 16:00 ZEU 160

Reduction of Noble Metal Ions to Metal Nanoparticles on J-Aggreates — •Stefan Kirstein[1], Hans v. Berlepsch[2], Christoph Böttcher[2], Dörthe M. Eisele[1], and Anna Burmistrova[1] — [1]Humboldt University of Berlin — [2]Free University, Berlin

Cyanine dye molecules and their J-aggregates are well known to serve as sensitizers for photo induced electron transfer processes. Technically, this feature is utilized in photographic films where dyes are adsorbed at silver halide crystals which is reduced to elemtary silver by an electron transfer from the photoexcited dye. Here, the same mechanism is used to grow silver nanoparticles at the surface of tubular J-aggregates form $AgNO_3$ salt solutions.

The amphiphilic tetrachlorobenzimidacarbocyanine dye molecule C8S3 (amphipipe) forms tubular J-aggregates in aqueous solutions with a uniform diameter of 17 nm and lengths of over 100 μm. The addition of noble metal salts (Na_2PdCl_4 or $AgNO_3$) to a solution of C8S3 aggregates leads to the formation of metal nanoparticles at the surface of the dye aggregates. The particles are observed by cryo-TEM and also by AFM for aggregates adsorbed at solid surfaces. The particles are rather uniform in size with a mean diameter of a few nanometer and distributed along the aggregate surface. In parallel to the growth of the particles a dramatic quenching of the aggregate fluorescence is observed. Therefore, the growth of the metal nanoparticles is explained by a photoexcited electron transfer process from the J-aggrgates to the metal ions. A systematic study of this process for $AgNO_3$ will be presented.

CPP 16.7 Wed 16:15 ZEU 160

Torsional Potentials for the Ground and Excited State of Bithiophene Calculated by Time-dependent Density Functional Theory — •Wichard J.D. Beenken[1], Sebastian Westenhoff[2], and Tõnu Pullerits[3] — [1]Technische Universität Ilmenau, FG Theoretische Physik I, Postfach 100565, D-98684 Ilmenau — [2]University of Cambridge, Optoelectronics Group, Cavendish Laboratory, CB3 0HE, UK — [3]Lunds Universitet, Kemisk Fysik, Box 124, SE-22100 Lund

We have studied bithiophene by time-dependent density functional theory. In particular we have analyzed the dependence of singlet excitation energies and transition dipoles on the torsional angle between the two thiophenyl groups. The torsional spectrum has been computed quantum-mechanically as well as semi-classically in order to understand, how this influences the broadening of absorption and luminescence spectra. We discuss the general consequences for the spectral broadening, Stokes shift and energy relaxation in poly-thiophenes, in particular, how torsional disorder effects the absorption and photoluminescence spectra. Furthermore, such results are necessary input parameters for molecular dynamics. In particular for simulation of polythiophenes in the excited state reliable data are rare. We will show some exemplary simulations.

CPP 16.8 Wed 16:30 ZEU 160

Optical Absorption and Energy Transport in Dendrimers — •Christoph Supritz[1], Petr Chvosta[2], and Peter Reineker[1] — [1]Department of Theoretical Physics, University of Ulm, 89069 Ulm — [2]Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, Prague

Dendrimers are highly branched polymers which are expected to be useful, for example, as efficient artificial light harvesting systems (like in photosynthesis) in nano-technological applications. It is generally assumed that inside dendrimers energy is transported via Frenkel excitons, but at the moment it is not clear whether this energy transport occurs in a coherent (wavelike) manner or via an incoherent hopping process. In our model we take into account the exciton phonon interaction by introducing a heat bath that interacts with the exciton in a stochastic manner. In this way we can describe the coupled coherent and incoherent exciton transport inside dendrimers and calculate their linear optical absorption spectra in the framework of linear response theory. To mimic the influence of a reaction center (like in photosynthesis) on energy transport, we attach a sink to the dendrimer through which excitons can be taken out of the system. We present these results for a number of different dendrimer types.

CPP 16.9 Wed 16:45 ZEU 160

Optical absorption of various linear and cyclic thiophene based π-conjugated polymers — •Mariusz Bednarz and Peter Reineker — Abteilung Theoretische Physik, Universität Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany

Recently, using thiophene based repeat units, the first series of fully conjugated macrocyclic structures: cyclo(thiophene-diacetylenes) and cyclo[n]thiophenes were synthesized (P. Bäuerle et al.). Such structures together with various series of linear oligothiophenes with controlled chain length exhibit an interesting relation between their absorption spectra. In particular, there is a clear relation between the peak position of the oligothiophenes and cyclothiophenes: the spectrum for the cyclothiphene with a given size corresponds to an oligotiophene chain of about half the length. The absorption spectra of such linear and cycliothiophenes show a systematic red shift with increasing number of thiophene units. In the present contribution, we will address an approach, based on the Frenkel exciton Hamiltonian, which describes the observed red shift tendency and the relationship between cyclothiophenes and corresponding oligothiophenes. Detailed study of the microscopic parameters depending on various side- and end-groups attached to the bare thiophene chains will be given. Also we show that cyclo(thiophene-diacetylenes) can be described as a fully conjugated system with very interesting manifestation of the cyclic symmetry as a Davydov components in the case of very small rings. It will be shown that diacetylene units embedded into thiophene cyclic structures can be described as another chromophor with larger $\pi - \pi*$ transition than thiophene units itself.

CPP 16.10 Wed 17:00 ZEU 160

Amplified Spontaneous Emission of Cross-linkable Conjugated Polymers in Multilayer Devices — •Bodo Wallikewitz, Dirk Hertel, and Klaus Meerholz — Universität zu Köln, Luxemburgerstrasse 116, 50939 Köln

Although the performance of polymer and small organic light emitting diodes (OLEDs) has made tremendous progress over the past decade, electrically pumped organic laser diodes as an advanced application remain a challenge. To achieve lasing optical gain manifested by for instance amplified spontaneous emission (ASE) is mandatory. We investigated for the first time ASE properties, gain and loss of cross-linked conjugated copolymers. Cross-linkable materials offer the advantage of solution processing of thick multilayer devices, essential for future electric driven organic lasers. Furthermore we studied the influence of chromophore type and chromophore concentration on the ASE threshold, optical gain and loss. We obtained low thresholds below 5 uJ/cm2, high gain above 33 cm-1 and low losses below 5 cm-1. These are very low thresholds, even for conventional conjugated polymers described in the literature. Thick hole transport layers (HTL) are necessary to enable ASE and optimize mode confinement in the emitter material on quenching electrodes. We restored the properties of neat polymer films on electrodes by using a thick, cross-linked HTL in between. The threshold is minimized by optimizing the refractive index of HTL, HTL thickness and polymer thickness. Furthermore, electrical properties of HTLs and efficiencies of thick multilayer OLEDs are presented and discussed.

CPP 16.11 Wed 17:15 ZEU 160

Watching protons tunnel: Nuclear momentum distributions from electronic structure calculations — •Daniel Sebastiani — MPI Polymerforschung; Ackermannweg 10; 55128 Mainz

We present first-principles electronic structure calculations of nuclear momentum densities $\rho_n(\mathbf{p}) = |\mathbf{\Psi_n(p)}|^\mathbf{2}$ (where $\Psi_n(\mathbf{p})$ is the nuclear vibrational wavefunction in momentum representation). Experimentally, the momentum distributions $\rho_n(\mathbf{p})$ are directly accessible through neutron Compton scattering methods. Our computational technique can be applied to complex hydrogen bonded systems (molecules or condensed phases). We illustrate its potential by describing the tunneling-induced ferroelectric phase transition in potassium dihydrogen phosphate (KDP). The results are in very good agreement with experiment.