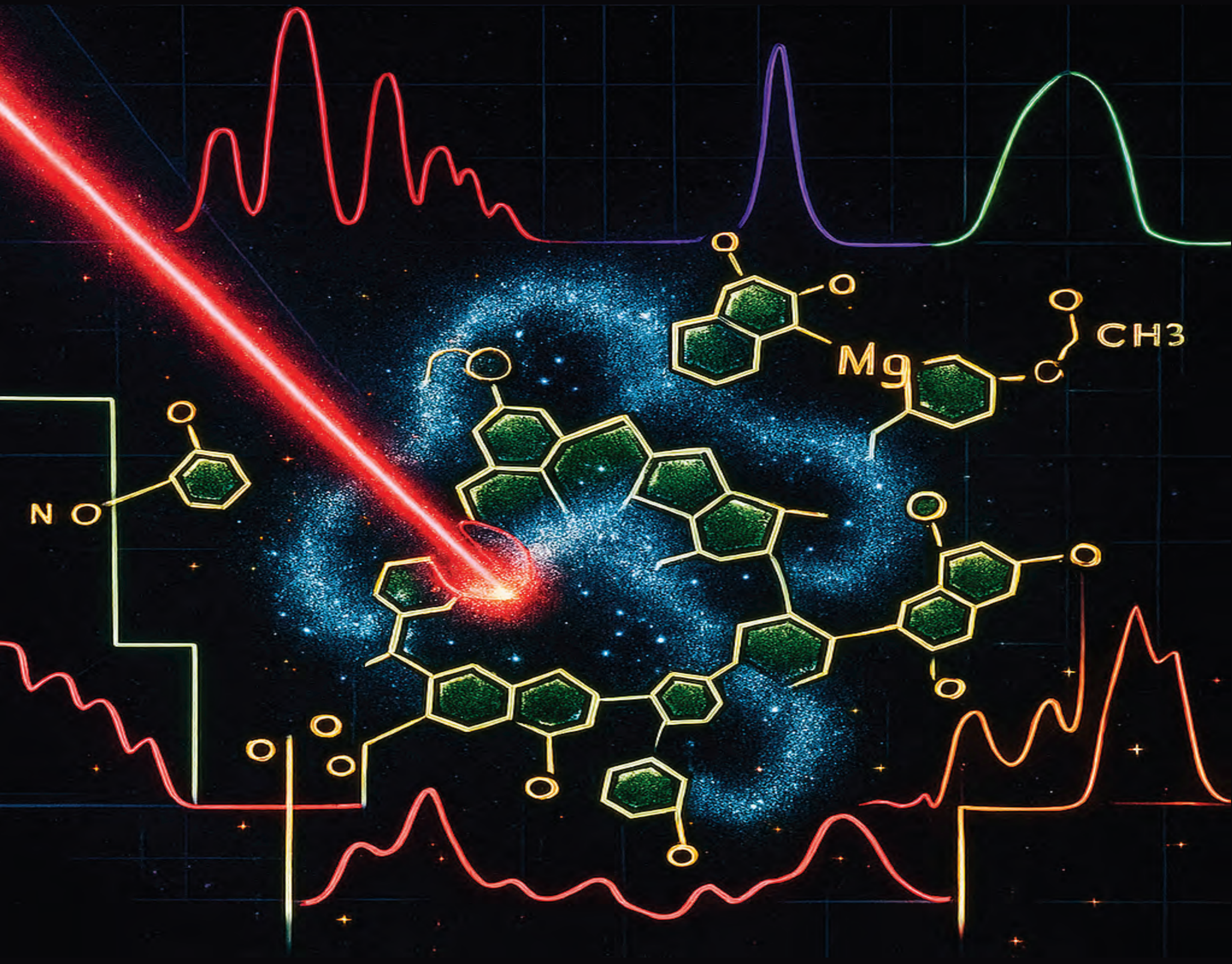
EXTENDED HANSEATIC MEETING ON
EXCITON DYNAMICS & SPECTROSCOPY



Program and Abstracts

VILNIUS, LITHUANIA

29 September – 3 October, 2025

Welcome

The Organizing Committee welcomes you to Extended Hanseatic Workshops on ***Exciton Dynamics and Spectroscopy***, **EEDS2025**. It is a continuation and extension of exciton (EXC) workshop, which was held in Rostock, Germany (2011–2018) and in Vilnius, Lithuania (2022). The conference attracts researchers and students from the Baltic region (and beyond) to discuss optical excitation dynamics and relaxation in molecules, nanoparticles and extended pure and hybrid complex systems, as well as optical spectroscopy in general, ranging from molecules, molecular aggregates, synthetic devices to photosynthesis in Nature.

This time, the Workshop is divided into three parts:

September 29	International HPC competence workshop
September 30–October 2	Exciton dynamics and spectroscopy: experiment and theory
October 2–3	Doctoral Network *Photosynthetic Antennas in a Computational Microscope* (PhotoCaM) workshop

Organizing Committee (Vilnius University)

Darius Abramavičius

Mindaugas Mačernis

Vytautas Bubilaitis

Laura Baliulytė

Program Committee

Tomáš Mančal (Charles University, Czech Republic)

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Darius Abramavičius (Vilnius University, Lithuania)

Mindaugas Mačernis (Vilnius University, Lithuania)

Ulrich Kleinekathöfer (Constructor University, Germany)

Venue

National Center for Physical Sciences and Technology, Room A101, Saulėtekio Ave. 3,
LT-10257 Vilnius, Lithuania

Program

September 29

HPC-related presentations and training

10:00–11:00	Registration, HPC consultation, and coffee
Presentations	
11:00–11:30	**STEPAS TOLIAUTAS** | Artificial Intelligence
11:30–12:00	**VYTAUTAS BUBILAITIS** | Matlab and Julia
12:00–12:30	**DARIUS ABRAMAVICIUS** | QCFP
12:30–13:00	**JUOZAS ŠULSKUS** | HPC tools
13:00–14:00	Lunch
HPC Training	
14:00–15:30	**MINDAUGAS MACERNIS** | HPC Examples
15:30–16:00	Coffee Break
16:00–17:00	HPC Training-Tutorial

September 30

Session 1. Spectroscopy	
9:00–9:30	**Andrius Gelzinis** | Fourth Order Corrections for Absorption Calculations with Complex Time-Dependent Redfield Theory
9:30–10:00	**Joachim Seibt** | Theory of Photosystem I Single-Molecule Excitation–Emission Spectroscopy
10:00–10:30	**Bruno Robert** | Structure and Vibrational Landscape of Excitons in Photosynthetic Proteins
10:30–11:00	Coffee Break
Session 2. Quantumness	
11:00–11:30	**Thorsten Hansen** | Non-Normal Operators in Lindblad Equation for Exciton Dynamics, and Modified Redfield Simulation of Photo-Induced Electron Transfer
11:30–12:00	**Jacob Pedersen** | Time-Dependent Particle-Breaking Hartree–Fock Model for Electronically Open Molecules
12:00–12:30	**Nicola Lorenzoni** | Full Microscopic Simulations Uncover Persistent Quantum Effects in Primary Photosynthesis
12:30–13:00	**Leonas Valkunas** | Fuorescence Variability of Stilbene Aggregates and Heterostructured Films
13:00–14:00	Lunch
Session 3. Crystallites	
14:00–14:30	**Mindaugas Macernis** | Trans-stilbene Spectral Property Changes Compared to Polyene Models and Carotenoids: a Correlated Excited State Methods Approach
14:30–15:00	**Egidijus Vilčiauskas** | Modeling of Stilbene Complexes with Polystyrene by Using Molecular Dynamics
15:00–15:30	**Rokas Dobužinskas** | X-ray Diffraction and Exposure Studies on Functional Materials and Biological Systems: A Collaborative Research
15:30–16:00	Coffee Break
16:00–18:00	Posters

October 1

Session 4. Multiscale Dynamics	
9:00–9:30	**Thomas L.C. Jansen** | Coarse-Grained 2DES Simulations from Femtoseconds to Nanoseconds
9:30–10:00	**Ulrich Kleinekathöfer** | Multiscale Simulation of Light Harvesting in Algae and in Porphyrin-Clay Systems
10:00–10:30	**Maxim S. Pshenichnikov** | Exciton Dynamics in Artificial Light-Harvesting Complexes: Bridging Experiment and Theory
10:30–11:00	Coffee Break
Session 5. Artificial Systems	
11:00–11:30	**Laura Baliulyte** | Theoretical Modelling of $TPPS_4$ Aggregation
11:30–12:00	**Alytis Gruodis** | $TPPS_4$ and $TPPS_3$ Protonation: Molecular Structure Modeling Using Quantum Chemistry Methods
12:00–12:30	**Eimantas Urniežius** | Modeling of $TPPS_4$ Nanotubes and their Optical Spectra
12:30–13:00	Free Time
13:00–14:00	Lunch
14:00–17:00	Free Time / Excursions
17:00	Conference Dinner (Novotel Hotel)

October 2

Session 6. Complexity	
9:00–9:30	**Thomas Renger** | Theory of Primary Processes in Photosynthetic Reaction Centers
9:30–10:00	**Vangelis Daskalakis** | Intrinsic Conformational Plasticity Fine-Tunes Light Harvesting in Diatoms
10:00–10:30	**Gabrielė Rankelytė** | Impact of the Protein Environment on the Excited States of the Pigments in Photosynthetic Complexes
10:30–11:00	Coffee Break
Session 7. Many-Body	
11:00–11:30	**Pavel Malý** | Multi-Exciton Spectra and Dynamics in Fifth-Order Transient Absorption Spectroscopy
11:30–12:00	**Malcolm Garrow** | Ultrafast Fluorescence-Detected Transient Absorption Microscopy
12:00–12:30	**Valdas Šablinskas** | Matrix Isolation FTIR Spectroscopy of Hydrogen Bonding and Conformational Dynamics in Short-Chain Monocarboxylic Acid
12:30–12:45	**Joel Santos** | Multiscale Modeling of Energy Transport for Light-Harvesting and Non-Photochemical Quenching in Higher Plants
12:45–13:00	**Arunjyoti Baidya** | A Unified Framework for Coupled Exciton-Phonon Dynamics using Generalized Nonlinear Exciton Equations
13:00–14:00	Lunch
14:00–14:15	**Boutheina Zender** | Predicting Structure–Function Correlation in Light Harvesting Complexes of Diatoms via Computational Approaches
14:15–15:30	Short poster presentations (5–10 min each)
15:30–16:00	Coffee Break
16:00–18:00	Posters

October 3

PhotoCam Entrepreneurship Workshop: From Lab to Market

Student Training	
9:00–9:15	Welcome & Introduction
9:15–10:15	**SESSION 1** | From Invention to Impact (Different ways how inventions could reach their applicability: theory and case study)
10:15–11:15	**SESSION 2** | Intellectual Property 101 (Basics of intellectual property and why it is important for researchers:theory and case study)
11:15–11:30	Coffee Break
11:30–12:30	**SESSION 3** | Market Thinking for Researchers (Who are the target users of your invention, and how to address them: theory and case study)
12:30–13:30	Lunch
13:30–14:15	**SESSION 4** | From Research to Startup (Applying research through developing a startup and understanding how they operate)
14:15–15:45	**SESSION 5** | Idea sprint—Pitch Your Idea (Practice: developing concepts around research-based ideas in groups and preparing short pitches)
15:45–16:00	Coffee Break
16:00–17:00	**SESSION 6** | Pitching & Feedback (Pitching ideas and exchanging feedback)

Poster Presentations

P1	David V. Rubio | Multiscale Simulation of the Fucoxanthin Chlorophyll *a*/*c* Protein Complex from the Diatom *C. Gracilis*
P2	Ebru Akkus | Elucidating the Exciton Transfer Mechanism in LHCII through Machine Learning
P3	Mustafa Ozdemir | Quantum Chemical Comparison of Photosynthetic Special Pairs
P4	Gregor Hill | Molecular Determinants of the Mechanism of Action of PSBS under the Computational Microscope
P5	Krishna P. Siwakoti | Theory of Charge Transfer and Primary Electron Transfer in Open and Closed Reaction Centers of Photosystem II
P6	Valentin Gradisteanu | pKa Prediction for LHC Residues, in the Presence of LHC-Protein and LHC-Carotenoid, Lipid Interactions
P7	Stephanie C.G. Migoni | Fluorescence-Detected Two-Dimensional Spectroscopy of Exciton Dynamics and Annihilation Using Coarse-Grained Simulations
P8	G.A.H. ten Hoven | Fourth Order Extension of Exciton Population Transfer Rates
P9	Dongyu Lyu | Protonation State and Structural Control of Exciton Transfer in Cryptophytes
P10	Maurice Schenker | Shedding Light on the Excited State Dynamics of DNA-Templated Silver Nanoclusters
P11	Michal Ptáček | Generalized Description of Non-Adiabatic Dissipative Energy Dynamics in Porphyrin Derivatives
P12	Matteo Bruschi | Influence of the Energetic Landscape on Multi-Exciton Energy Transfer and Annihilation
P13	Rugilė Žalkauskaitė | Interfacing X-Ray Diffraction (XRD) and Molecular Dynamics Modeling for Amorphous Molecular Systems
P14	Austėja Mikalčiūtė | Complete Exciton Hamiltonian for Photosynthetic Pigment–Protein Complexes
P15	Rokas Garbacauskas | Using Transformer Neural Networks to Speed up Molecular Structure Optimization at DFT Level

Abstracts of Oral Presentations

Fourth Order Corrections for Absorption Calculations with Complex Time-Dependent Redfield Theory

Andrius Gelzinis[1,2] *and Leonas Valkunas*[1]

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Simulations of absorption spectra for molecular complexes remain important to this day. High accuracy, if compared to exact results, can be obtained using the complex time-dependent Redfield (ctR) theory. Nonetheless, in some cases there are some deviations. The ctR approach is based on the second order cumulant expansion. For Gaussian baths, this approach would be exact if only the diagonal energy fluctuations in excitonic basis were present. For coupled molecular systems, however, there are always off-diagonal fluctuations, which makes the ctR theory approximate. In this contribution, we investigate fourth order ctR corrections. In general, fourth order corrections involve four-dimensional time integrals, which increase the computational cost of the approach considerably. To mitigate this issue, we obtain analytical expressions for the fourth order corrections. This is possible using an exponential representation for the bath correlation function. To achieve this for any spectral density, we utilize the ESPRIT approach. In the presentation, we will analyze the accuracy of the fourth order ctR corrections for absorption calculations in a variety of parameter regimes.

Theory of Photosystem I Single-Molecule Excitation–Emission Spectroscopy

Joachim Seibt[1], *Xianjun Zhang*[2], *Yutaka Shibata*[2], *and Thomas Renger*[1]

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We developed a theoretical description of single-molecule excitation-emission spectroscopy (SMEES) in view of explaining effects observed in SMEES of the photosynthetic complex photosystem (PS) I, which consists of three PS I monomers with each of them containing 96 chlorophyll a (Chl a) pigments.

Our model of a PS I monomer involves excitonic coupling among the pigments and quenching due to non-radiative decay at the oxidized reaction center. Different regimes of perturbative treatment, identified by the relative size of excitonic couplings and couplings of the local electronic excitations to a heat bath, are accounted for by introducing exciton domains. In SMEES the frequency resolution with respect to excitation and emission is obtained by varying the frequency of an excitation pulse and by Fourier transformation, respectively. Between excitation and emission the excited-state populations created by the excitation pulse undergo transfer processes, which lead to a redistribution of populations in combination with quenching. Modifications of the local excitation energies (site energies) of the pigments due to interaction with the protein environment enter in terms of static disorder. Different mutual orientations between the external field and the single PS I complexes are taken into account by considering different propagation directions of the field.

It turned out that a variation of the orientation of PS I has less influence on the variability of the excitation-emission spectra (EES) than the variation of site energies, as the orientations only influence the relative peak intensities, while the site energies also determine the peak positions. Moreover, the site energies also gain influence on the preferential pathways of transfer toward two low-energy terminal emitter domains (TEDs) Low1 and Low2. To reproduce effects observed in SMEES experiments on PS I in different solvents, in particular the appearance of an inclination of the EES measured in polyvinyl alcohol (PVA), we modified the site energies of pigments in a PS I monomer at both interfaces to neighboring PS I monomers. We found that a correlated or anticorrelated appearance of the EES depends on whether or not the energetic ordering of the interfaces closer to Low1 and Low2 corresponds to the energetic ordering of the TEDs. In this way we demonstrated that SMEES is a promising tool to monitor energy transfer pathways in pigment-protein complexes.

Structure and Vibrational Landscape of Excitons in Photosynthetic Proteins

Bruno Robert[1], *Andrew Gall*[1], *Andy Pascal*[1], *James Sturgis*[2], *and Leonas Valkunas*[3]

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Excitation energy transfers in photosynthesis generally involve excitonically coupled (bacterio)chlorophyll molecules. It thus consists of exciton migration within and between photosynthetic proteins, the dynamics of which depends on the vibrational modes resonant with the energy gaps between the involved excited states. The structure and vibrational landscape of excitons thus constitute an essential knowledge to understand the amazing efficiency of photosynthesis. From fluorescence line narrowing spectra of excitons in light-harvesting proteins from purple photosynthetic bacteria, we extract information on how many bacteriochlorophylls the excitons reside and in which proportions, and on the conformation of these molecules.

Spectra of bacteriochlorophyll proteins appear to generally contain additional clear contributions between 200 and 1000 cm^{-1} as compared to isolated molecules, which must open additional excitation energy transfer channels for excitation transfers.

In chlorophyll-based antenna, exciton delocalization at low temperature is only observed when electronic coupling is larger than 90 wavenumbers. No additional vibrational modes at frequencies higher than 200 cm^{-1} are observed any of these proteins, suggesting a fundamentally different usage of vibrational assistance in excitation energy transfer between photosynthesis of purple bacteria and that of oxygenic organisms.

Non-Normal Operators in Lindblad Equation for Exciton Dynamics, and Modified Redfield Simulation of Photo-Induced Electron Transfer

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The distinction between normal and non-normal operators in dynamics is finding increasing usage in applied mathematics and engineering. We apply this distinction to the microscopic Lindblad equation for exciton dynamics. We use the matrix exponential norm as a proxy observable that can high-light non-normality. We show that pure dephasing is normal. Relaxation on the other hand is non-normal, meaning that is can be responsible for the emergence of intermediate time-scales in the dynamics. We venture a suggestion for a spectroscopic experiment that can display the non-normality of the dynamics.

In addition, we present a modified Redfield simulation of photo-induced charge transfer in a triad molecular system. Our simulations capture both of the two time-scales seen experimentally in the overall charge transfer process.

Time-Dependent Particle-Breaking Hartree–Fock Model for Electronically Open Molecules

Jacob Pedersen[1,2], *Bendik Støa Sannes*[2], *Regina Paul née Matveeva*[2], *Sonia Coriani*[1], *and Ida-Marie Høyvik*[2]

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We develop the time-dependent particle-breaking Hartree–Fock (TDPBHF) model to describe excited states and linear response properties of electronically open molecules. This work represents the first step towards building a wave-function-based response theory framework for electronically open quantum systems equivalent to that of closed quantum systems. In the limit of particle conservation, TDPBHF reduces to standard time-dependent Hartree–Fock (TDHF) theory. We illustrate the TDPBHF model by computing valence absorption spectra and frequency-dependent electric dipole polarizabilities for a set of small- to medium-sized organic molecules. The particle-breaking interactions are observed to non-uniformly redshift the excitation energies and induce qualitative changes in the absorption profile. In addition, the mixing of multiple excitations in the TDPBHF wave function is observed to dampen the divergence of the response function in the vicinity of resonance energies.

Full Microscopic Simulations Uncover Persistent Quantum Effects in Primary Photosynthesis

Nicola Lorenzoni, Thibaut Lacroix, James Lim, Dario Tamascelli, Susana F. Huelga, and Martin B. Plenio

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The presence of quantum effects in photosynthetic excitation energy transfer has been intensely debated over the past decade. Nonlinear spectroscopy cannot unambiguously distinguish coherent electronic dynamics from underdamped vibrational motion, and rigorous numerical simulations of realistic microscopic models have been intractable. Experimental studies supported by approximate numerical treatments that severely coarse-grain the vibrational environment have claimed the absence of long-lived quantum effects. Here, we report the first non-perturbative, accurate microscopic model simulations of the Fenna-Matthews-Olson photosynthetic complex and demonstrate the presence of long-lived excitonic coherences at 77 K and room temperature, which persist on picosecond time scales, similar to those of excitation energy transfer. Furthermore, we show that full microscopic simulations of nonlinear optical spectra are essential for identifying experimental evidence of quantum effects in photosynthesis, as approximate theoretical methods can misinterpret experimental data and potentially overlook quantum phenomena.

Fuorescence Variability of Stilbene Aggregates and Heterostructured Films

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Variety of organic molecules, especially diarylethylenes, due to the sensing abilities, is considered as promising components of highly sensitive instruments for various applications. A range of this type of molecules demonstrates specific photochemical properties, such as, for instance, trans-cis isomerization or variability of the fluorescence lifetime depending on environmental conditions. Stilbene is a classic example of such type of molecules [1]. For example, stilbene monocrystals have been used in scintillating devices, which demonstrate the ability to distinguish between effects caused by different illuminations [2]. In this presentation studies of the excitation dynamics in hot-pressed and in sublimated films of stilbene are considered in wide temperature range, from 15 K up to room temperature. The fluorescence spectra and their kinetics are analysed together with the time-resolved fluorescence measurements performed for the stilbene solutions in chloroform and for stilbene in polystyrene (PS) matrix. In opposite to the results obtained in solution and in PS matrix, where the excitation dynamics is controlled by molecular isomerization/twisting process, the fast exciton diffusion yields thermalized exciton distribution and a small number of fluorescence centres responsible for fluorescence line shape and timescale and their temperature dependencies of the bulk solids. The relevant theoretical description explaining these experimental observations based on quantum chemical calculations are analysed for the stilbene aggregates. The conclusions are also supported by purposeful fluorescence studies at different concentrations of stilbene molecules.

[1] D. H. Waldeck, Chem. Rev., 1991, 91, 415-436.
[2] S. K. Lee, Prog. Nuclear Sci. Techn., 2011, 292-295.

Trans-stilbene Spectral Property Changes Compared to Polyene Models and Carotenoids: a Correlated Excited State Methods Approach

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Stilbenes occur naturally in plants such as grapevines (e.g., resveratrol), while carotenoids (Cars) are abundant pigments in fruits, vegetables, and photosynthetic organisms, but their properties differ despite structural similarities [1–5]. This contrast between natural origin and structural resemblance forms the central focus of the present study.

Stilbene (1,2-diphenylethylene) consists of two aromatic rings bonded to a central carbon-carbon double bond, forming a conjugated polyene-type system. During isomerization, the phenyl rings twist around the single C–C bond, making stilbene molecules promising candidates for molecular switches [1]. Unusual temperature-dependent fluorescence of stilbenes was observed, highlighting the role of aggregation effects on spectral properties [2].

In contrast, carotenoids, although also polyene-based, display stronger symmetry distortions in their conjugated C=C chains, which significantly affect their electronic properties. According to the polyene model, the S_1 excited state has perturbed A_g^- symmetry and is optically forbidden from the ground state [3–5]. This contradicts predictions based on stilbene-like systems.

In this work, correlated excited-state methods were applied, specifically the ADC(n)-x family as implemented in the Q-Chem package, to resolve low-lying forbidden states. The approach was successfully benchmarked on short polyenes ($N = 5$). In addition, methodological aspects of AO basis reduction and normalization [6] were considered to ensure reliability in describing subtle differences between polyene and stilbene excited states.

Detailed results on the differences between stilbene and polyene models, and their connections to carotenoid excited-state properties, will be presented at the conference.

[1] V. Nagarajan et al., Condens. Matter Phys. 21, 43010–43012, 2018.
[2] R. Karpicz et al., Phys. Chem. Chem. Phys. 23, 3447–3454, 2021.
[3] T. Polívka, V. Sundström, Chem. Phys. Lett. 477 (2009) 1.
[4] M. Macernis, J. Sulskus, C.D. Duffy, A.V. Ruban, L. Valkunas, J. Phys. Chem. A 116 (2012) 9843.
[5] P. Tavan, K. Schulten, J. Chem. Phys. 85 (1986) 6602.
[6] M. Macernis, Phys. Chem. Chem. Phys. 27 (2025) 14555.

Modeling of Stilbene Complexes with Polystyrene by Using Molecular Dynamics

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Stilbene is a diarylethene which exhibits fluorescence and reversible photoisomerization upon UV excitation [1-2]. Despite extensive research, an atomistic examination of its condensed-phase conformations remains limited. The influence of the environment on stilbene geometry was investigated in crystalline, disordered, and styrene oligomer–encapsulated states using a combined molecular dynamic (MD) and quantum mechanics (QM) approach.

MD simulations with GROMACS revealed distinct dihedral behaviors across systems: pronounced fluctuations (~180° twisting) in disordered stilbene, modest but consistent deviations in the crystalline phase, and significant, stable offsets in oligomer environments, indicating strong conformational restraint. Potential energy surface scans at the B3LYP/cc-pVDZ and PM6-D3 levels showed a phenyl twist of dihedral angle $\vartheta \approx 162$–$165°$ in oligomer environments (vs. 180° in vacuum case) and a dihedral angle of $\vartheta \approx 175°$ in crystal, with steeper energy gradients under confinement.

This twisting behavior suggests the emergence of barriers hindering π–π stacking and crystallization. BSSE-corrected complexation energies (0.026–0.051 eV) were calculated for stilbene between styrene dodecamers, proportional to the degree of twist. Accelerated weighted histogram (AWH) free-energy simulations yielded a thermodynamically favorable Gibbs free energy of –0.22 eV for insertion into a dodecamer matrix. Results are consistent with experimental observations of suppressed crystallization in low-concentration stilbene-polystyrene mixtures, and demonstrate the strength of combining MD and QM for probing multi-phase molecular systems. Detailed results on the differences between stilbene-polystyrene models will be presented at the conference.

[1] V. Nagarajan et al., Condens. Matter Phys. 21, 43010–43012, 2018.
[2] R. Karpicz et al., Phys. Chem. Chem. Phys. 23, 3447–3454, 2021.

X-ray Diffraction and Exposure Studies on Functional Materials and Biological Systems: A Collaborative Research

Rokas Dobužinskas[1], *Mindaugas Mačernis*[1], *Gytis Sliaužys*[1], *Romualdas Čepas*[1], *Ūla Marija Lauciūtė*[2], *Mantas Grigalavičius*[2], *Eglė Martinaitytė*[3], *Šarūnas Svirskas*[3], *Žygimantas Logminas*[3], *Artyom Plyushch*[3], *Gediminas Usevičius*[3], *Mantas Šimėnas*[3], *Renata Karpič*[4], *and Darius Abramavičius*[1]

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The X-ray Laboratory at the Institute of Chemical Physics serves as a collaborative hub for advanced research on structural characterization and radiation–matter interactions. This presentation summarizes recent results obtained in partnership with multiple scientific groups, focusing on three interconnected directions: (i) X-ray diffraction studies of advanced functional materials, (ii) controlled X-ray exposure of biological systems, and (iii) defect formation in perovskites under hard X-ray illumination.

In the first part, we present diffraction-based investigations of lead-free ferroelectric ceramics, chemical vapor deposition (CVD) diamond layers, and organic–polymer composites incorporating stilbene mixtures in polystyrene. High-resolution measurements reveal correlations between synthesis conditions, crystallographic features, and functional properties, providing insights into phase stability, lattice distortions, and texture evolution.

The second part addresses radiobiological effects of X-ray exposure. Cancerous cell cultures were irradiated under controlled conditions to evaluate dose-rate dependencies relevant to cancer radiotherapy and to assess post-irradiation viability. These studies contribute to understanding cellular response mechanisms and optimizing therapeutic protocols.

Finally, we explore the impact of hard X-ray illumination on hybrid perovskite materials, where induced structural defects were detected via electron paramagnetic resonance (EPR) spectroscopy. This approach provides a unique perspective on defect dynamics and their implications for optoelectronic performance using high dose radiation.

By integrating structural, radiobiological, and defect-formation studies, this work demonstrates the dual role of X-rays as both a diagnostic probe and a controlled stimulus. The results highlight the importance of shared infrastructure and interdisciplinary collaboration in addressing challenges at the interface of materials science, radiation physics, and life sciences.

Coarse-Grained 2DES Simulations from Femtoseconds to Nanoseconds

Kai Zhong[1,2], *Hoang Long Nguyen*[1,2], *Thanh Nhut Do*[2], *Howe-Siang Tan*[2],
Jasper Knoester[1,3], *and Thomas L.C. Jansen*[1]

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Two-Dimensional Electronic Spectroscopy (2DES) is a powerful technique for probing exciton and charge separation dynamics in photosynthetic light-harvesting systems. While many studies focus on isolated complexes, recent work highlights the significant role of inter-complex interactions within functional super-complexes in modulating energy transfer and coherence phenomena [1]. Understanding such multiscale behavior requires both experimental and theoretical approaches that span large systems and a wide range of timescales.

We present a novel and efficient coarse-grained spectral simulation protocol [2] that enables the calculation of 2DES across diverse dynamical regimes—from ultrafast coherent motion (∼100 fs) to slower incoherent relaxation and trapping (up to 1 ns)—without an increase in computational cost when simulating multiple waiting times.

The method partitions chromophores into strongly coupled segments, allowing coherent dynamics within each segment and incoherent dynamics between them. Segment dynamics are assumed uncorrelated, enabling a hybrid modeling approach: the time-dependent multi-chromophoric Förster resonance energy transfer (MC-FRET) method [3] is used to describe the waiting time evolution, while response functions based on the doorway-window formalism capture the coherence periods. This framework allows for a flexible and computationally tractable simulation of 2DES that is well suited for large photosynthetic assemblies.

We demonstrate the capabilities of the approach on the LH2 complex from purple bacteria, where it reproduces key features of the anisotropy decay from femtoseconds to picoseconds [2], validating both accuracy and efficiency. We also discuss its application to the larger PSII super-complex from higher plants, showing how the method can guide spectral interpretation, identify energy transfer pathways, and reveal exciton traps and sinks.

This coarse-grained approach opens the door to systematic simulations of 2DES on a scale and timespan previously inaccessible, enabling new insights into light-harvesting dynamics in complex biological systems.

[1] Sci. Adv. 2024, 10, eadh0911.
[2] J. Chem. Theory Comput. 2024, 20, 6111–6124.
[3] J. Chem. Theory Comput. 2025, 21, 254–266.

Multiscale Simulation of Light Harvesting in Algae and in Porphyrin-Clay Systems

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Natural light-harvesting antenna complexes efficiently capture solar energy mostly using chlorophyll molecules, i.e., magnesium porphyrin pigments, embedded in a protein matrix. This is also the case in diatoms which are one of the most abundant photosynthetic organisms on earth and contribute largely to atmospheric oxygen production. At the same time, and inspired by such natural configurations, artificial clay-porphyrin antenna structures have experimentally been synthesized and demonstrated to exhibit remarkable excitation energy transfer properties. The current study presents a state-of-the-art multiscale simulation protocol which can be applied to both biological and man-made light-harvesting systems. Diatoms contain fucoxanthin and chlorophyll-a/c binding proteins (FCPs) as light-harvesting complexes with a remarkable adaptation to the fluctuating light on ocean surfaces. To understand the basis of the photosynthetic process in diatoms, the excitation energy funneling within FCPs was analyzed in detail. A similar technique was employed to simulate a synthetic light-harvesting system that emulates natural mechanisms by arranging cationic free-base porphyrin molecules on an anionic clay surface. To improve the accuracy of our results, we incorporated an innovative multifidelity machine learning approach, which allows the prediction of excitation energies at a numerically demanding time-dependent density functional theory level.

Exciton Dynamics in Artificial Light-Harvesting Complexes: Bridging Experiment and Theory

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Natural light-harvesting antennae, ubiquitous in photosynthetic organisms such as green algae and bacteria, are renowned for their exceptional energy transfer efficiency, enabled by densely packed, strongly interacting chromophores. This structural organization facilitates the formation of delocalized Frenkel excitons, which migrate coherently along the antenna complex, enabling highly efficient excitation energy transfer [1]. Molecular double-walled nanotubes (DWNTs), self-assembled from amphiphilic C8S3 dye molecules in aqueous solution, serve as a well-defined biomimetic model system for investigating such excitonic processes. Despite their soft molecular nature, DWNTs exhibit an exceptionally low degree of structural disorder, allowing for exciton delocalization across hundreds of chromophores.

To fully harness the potential of these systems, two central challenges must be addressed. First, quantum-classical theoretical models must accurately capture the underlying excitonic structure and dynamics in order to predict experimentally accessible optical observables. Second, experimental techniques must be designed to yield spectroscopic data that enable direct and quantitative comparison with theoretical predictions.

Here, we present two recent examples that bridge theory and experiment. First, by combining theoretical analysis with polarization-resolved photoluminescence microscopy of individual DWNTs, we demonstrate that the transition dipole moments of the emitting excitons are confined within a narrow angular range aligned along the nanotube axis. This behavior arises from negative intermolecular couplings that produce exciton states with wavefunction coefficients all in phase, yielding a reduced linear dichroism approaching unity [2]. Second, using two-dimensional and time-resolved photoluminescence spectroscopy, we show that Frenkel excitons in DWNTs maintain extensive delocalization even in the presence of embedded molecular substitutional dopants acting as deep energetic traps. Theoretical simulations reproduce the observed dynamics and reveal that excitons adaptively redistribute to circumvent trap sites [3]. These findings underscore the robustness of supramolecular architectures for supporting efficient exciton transport under fabrication-relevant conditions.

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Theoretical Modelling of $TPPS_4$ Aggregation

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Recently, there has been growing interest in $TPPS_4$ for applications in photodynamic therapy as photosensibilizator [1]. The monomers of this porphyrin efficiently self-associate into H- and J-aggregates in aqueous media. It is not fully understood what kind of $TPPS_4$ configurations are building blocks of molecular aggregates. The goal of this study is to determine the most stable $TPPS_4$ dimers and tetramers.

The structures of $TPPS_4$ monomers and dimers were determined using DFT CAM-B3LYP/6-31G(d,p) method. PCM was used to evaluate the influence of water. In this research, the Gaussian 16 C.01 program [2] was used.

Based on our results, it can be said that the formation of zwitterionic dimers is the most probable. Due to this reason, the next part of this research was to determine zwitterionic tetramers. First of all, QM and MM calculations of $TPPS_4$ were performed. GAFF has parameters for most organic molecules [3]. However, for some molecular systems, the parameters must be revised due to the extended conjugation of C=C bonds in pigments [4]. Since $TPPS_4$ has a complex electron delocalization, it is necessary to adjust the FF parameters. In the present case [5], several parameters were adjusted for bonded interactions for both Z1 and Z2 zwitterions.

The second step was to construct Z1 and Z2 tetramers. The obtained tetramers were solvated with water boxes. Then, an MD simulation was performed with the AMBER 22 program. It was determined that there were two Z1 and Z2 linear tetramers. A comparison was performed of Z1 and Z2 tetramers' absorption spectra with the measured spectra from the previously published article [6]. Our analysis of results demonstrates that larger peak shifts of the Z1 tetramer's spectra are more similar to the experimental data; however, other configurations can be possible as well.

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Modeling of $TPPS_4$ Nanotubes and their Optical Spectra

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Large organic molecular aggregates have promising applications as nonlinear optical elements, active materials in photodynamic therapy, and other photonic technologies [1]. In particular, the porphyrin $TPPS_4$ forms two zwitterionic species (Z1 and Z2) at pH=1, which self-assemble into molecular nanotubes that can exist in left-handed (M) or right-handed (P) forms, exhibiting notable optical properties [2]. Although the macroscopic structure of these nanotubes is well studied, their microscopic structure - including the molecular orientation - remains poorly understood. This study develops a theoretical model of these nanotubes and employs the Frenkel excitonic framework to optimize their microscopic arrangement by reproducing their linear optical spectra.

The nanotube is modeled by constructing a 2D crystal lattice with a constant of $a = 9.3\,\text{Å}$, which is then rolled into a cylinder to form a tubular lattice of equally spaced points. A molecule is assigned to each point, each with four optical transition energies (two for the B band and two for the Q band), characterized by optical transition dipole vectors. Due to the molecule's planar symmetry, all dipole vectors lie within a defined molecular plane, whose orientation is described by a normal vector $\boldsymbol{n}$. Optical spectra are calculated by constructing the nanotube's Hamiltonian and solving the stationary Schrödinger equation to determine transition energies and wavefunctions. Optimization of the molecular plane's orientation is achieved by introducing two parameters, α_1 and α_2, which rotate the plane of each molecule relative to its lattice site.

By fitting simulated absorption spectra to experimental data, optimal values of $\alpha_1 = 32°$ and $\alpha_2 = 26°$ were obtained. In addition to absorption, circular dichroism (CD) spectra were calculated for both M and P-type nanotubes in the B band, yielding results that closely match experimental measurements. Furthermore, spectra of partially formed nanotubes were simulated, revealing the dynamic evolution of spectral peaks with increasing tube size and number of windings. To improve the model's accuracy, the effects of diagonal disorder were also incorporated into the spectral calculations.

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$TPPS_4$ and $TPPS_3$ Protonation: Molecular Structure Modeling Using Quantum Chemistry Methods

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In photodynamic therapy, 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin ($TPPS_4$) and 5,10,15-tris(4-sulfonatophenyl)-20-phenylporphyrin ($TPPS_3$) are well-known as nonlinear optic materials and photosensitizers. Optical absorption in the phototherapeutic window is sensitive due to various pH and pKa values of the surrounding in aqua media, where TPPS protonation and TPPS self-aggregations processes take place. Intermolecular interactions between SO_3- group and protonated central core lead formation of a simple dimer. Following interactions (dimer + monomer *etc*.) form J-aggregates (trimers, quarters, etc). Quantum chemical simulation of the TPPS structure have been provided using Gaussian 16 package. For simulation purposes, different TPPS monomers, dimers, trimers and sextamers were constructed using different protonation level related to the surrounding media pH: a) core and tails unprotonated (pH=7), b) core protonated, tails unprotonated (pH=4), c) core and tails protonated (pH=–1). Optimization of the ground electronic state has been provided using semiempirical CAM-B3LYP method and 6-31G(d) basis set consisting of polarization function (d). Electronic excitations were calculated using semiempirical TD method for singlets only. Environmental effects were included using PCM (water) routine for structure simulations as well as for excitations. Successful result of ground state energy optimization procedure allows us concluding that after protonation of the molecular core, molecular conformation (in the core pentaring area) changes from planar to the non-planar orientation (long pentaring axis from 0 deg to 25 deg). Phenyl ring orientation is chaotic, as located in the interval (40, 60) deg without strongly defined direction. Aggregates of core-to-tail type (dimers, trimers etc) could be formed using two TPPS monomers (core protonated, tails unprotonated) due to electrostatic interactions. Simulation of electronic excitations allows concluding excitation localization area. For transitions (population of excited "spectroscopic" state) corresponding to the well-known Soret band and Q-band, localization area is limited by three monomer unit in the sextamer aggregate.

Theory of Primary Processes in Photosynthetic Reaction Centers

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Certain cyanobacteria adopt to far-red light by incorporating a few chlorophyll *f* (Chl *f*) pigments in their photosystems. It has been controversially discussed in the literature, whether there is a Chl *f* in the reaction center (RC) of photosystem I (PSI). Although from a functional point of view, a low-energy Chl in the RC would be beneficial, earlier cryo-EM studies did not find any evidence for a Chl *f* in the RC. I will present such evidence from calculations of optical difference spectra (light-minus-dark) and note that the Rutherford group (Imperial College London, UK) has found independent evidence from cryo-EM, using an improved analysis.

In the second part of my talk I want to discuss primary electron transfer in open and closed photosystem II reaction centers. From QM/MM calculations on the Pheo-D1/Chl-D1 dimer and a subsequent diabatization, charge transfer, local excited states and their couplings are obtained.

These quantities are used to predict time constants for primary electron transfer, which are in good qualitative agreement with values predicted earlier based on time-resolved fluorescence data and structure-based energy transfer calculations.

Intrinsic Conformational Plasticity Fine-Tunes Light Harvesting in Diatoms

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Diatoms, photosynthetic eukaryotic phytoplankton, contribute a substantial portion (~25%) of global oxygen production. Their light-harvesting complexes (LHCs) exhibit diverse forms – from monomers to oligomers – yet the functional basis for this diversity is not clear. In this study, we explore the configurational landscape of LHCs from *Phaeodactylum tricornutum* and *Chaetoceros gracilis* using microsecond-scale all-atom molecular dynamics and Markov state modeling. Our analysis reveals distinct conformations that correspond to all experimentally resolved structures to date. By combining these structural ensembles with machine learning predictions, we show that conformational switching fine-tunes pigment–pigment exciton couplings, thereby modulating transitions between light-harvesting and photoprotective states via scaffold contraction and expansion – an intrinsic property that may be engineered. Overall, our findings support the idea that conformational differences in resolved LHCs across diatom species reflect proteins captured in different light acclimation states, advancing our understanding of photosynthetic regulation.

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Impact of the Protein Environment on the Excited States of the Pigments in Photosynthetic Complexes

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The most efficient organisms that carry out photosynthesis are higher plants. Photosystem I (PSI) is the most efficient light-to-energy conversion apparatus where almost all light, absorbed by the light harvesting antenna LHCI, is converted to chemical energy. In plants, light harvesting antenna of PSI is composed of four species of LHCI complexes. They all have very similar structure; however, their spectral properties are different. The excitation dynamics in LHCI are highly affected by the charge-transfer (CT) states that occur between the pigments. Known charge-transfer sites in LHCI do not completely explain the spectral properties of this antenna suggesting the presence of more CT states. The energy of these states is affected by the surrounding environment (pigments and protein). In our work, we investigated the LHCI of PSI complex structure, available at Protein Data Bank (PDB ID: 5L8R). Properties of the excited states of the pigments were calculated using "VU HPC" Saulėtekis supercomputer. Charge-density coupling method was used to evaluate excited state energy shifts, caused by the electrostatic environment. The results of the CDC method were compared to the results of QC calculations performed directly in the field of electrostatic charges. Our findings demonstrate the sensitivity of pigment excited state properties to changes in the surrounding environmental geometry (charge placement) and protein protonation pattern.

Multi-Exciton Spectra and Dynamics in Fifth-Order Transient Absorption Spectroscopy

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Recent developments in highly nonlinear transient absorption and two-dimensional electronic spectroscopy have brought renewed interest in multi-exciton dynamics and interaction [1]. Utilizing phase or intensity modulation or interferometric scanning, spectra of increasingly nonlinear order in interaction with light can be acquired simultaneously. The perturbative description is thus not merely a theoretical approach but a feature of the experiment, systematically probing increasingly higher number of excited particles.

Several points have been discussed in the recent literature, such as the 5th-order transient dynamics directly reflecting the exciton–exciton annihilation (EEA) [2], the EEA being coherently modified in H/J aggregates [3], or multi-excitonic states exhibiting quantum entanglement beyond simple change of basis [4]. Furthermore, EEA is often used as a probe of long-range exciton diffusive transport [2], described by bulk excitation density and with assumptions regarding exciton interaction [5].

Combining fifth-order nonlinear response theory with open-quantum system dynamics, we investigate these points, and the manifestation of such effects in highly nonlinear transient absorption. We focus on the influence of the aggregate geometry and the resulting electronic transition coupling on the bi-exciton state structure, transport dynamics and interaction. We find that spectrally-resolved highly-nonlinear transient absorption probes up to three-exciton states, is sensitive to the multi-exciton state structure, and reflects the interplay of exciton transport and EEA. The trends in the calculated transient spectra are directly compared to those observed in experimental data on molecular aggregates of varying geometry and disorder.

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Ultrafast Fluorescence-Detected Transient Absorption Microscopy

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Recently, our group has developed an extension to the technique of fluorescence lifetime imaging microscopy (FLIM) by introducing a broadband interferometric two-pulse excitation [1]. This allows for a spatially resolved measurement of the sample by correlating the excitation spectrum with the emission lifetime using an approach well known from Fourier transform spectroscopy. Thus, the experimental technique of interferometric excitation fluorescence lifetime imaging microscopy (ixFLIM) was created. Due to the possibility of correlating the excitation spectrum with the fluorescence lifetime, ixFLIM can enjoy the advantages of being able to monitor the formation of complexes or energy transfer mechanisms within a complex, for example.

Now, we have developed a new variant of fluorescence pump-probe (F-PP) spectroscopy that incorporates the advanced imaging offered by the ixFLIM technique, which we have called fluorescence-detected transient absorption microscopy (FluoTRAM). This was achieved with the addition of a wavelength-tuneable pump beam, using an optical parametric oscillator (OPO), to the ixFLIM setup. This presentation will thus discuss the main features and design of this new experimental setup, including the ixFLIM foundation. Two proof-of-concept measurements will also be presented, the first being a mixture of two fluorescent dyes in aqueous solution, cresyl violet and oxonol VI. This dye mixture makes for a good test for the experiment. Firstly, as the two dyes have very similar absorption and emission wavelengths within the visible range of light, but have two significantly different emission lifetimes, the ixFLIM part of the setup can distinguish them individually within the sample. The F-PP can then produce the pump-probe signals from each individual dye, so the ultrafast dynamics (such as ultrafast Stokes shifts, for example) can be determined where the photon counting method from the ixFLIM could not. The second proof-of-concept measurement presented will be the imaging of ultrafast excitation dynamics within a single chloroplast in a spinach leaf. This further explores the potential offered by the spatial resolution offered by the FluoTRAM instrument, as the xyz positioning of the imaging is offered by the microscopy along with the fluorescence lifetimes and transient excitation spectra. Finally, a brief discussion of potential applications of this setup will be offered.

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Matrix Isolation FTIR Spectroscopy of Hydrogen Bonding and Conformational Dynamics in Short-Chain Monocarboxylic Acid

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It is widely accepted that hydrogen bonding and conformational transitions in molecular compounds can be efficiently investigated by means of infrared spectroscopy. Such studies relay on unique spectral signatures of vibrational spectra of different conformers or molecular complexes. Unfortunately, the spectral differences in many cases are difficult to observe due to overlapping of the vibrational spectral bands. Low temperature matrix isolation spectroscopic technique in many cases allows to suppress such overlapping. Some results of studies of conformational dynamics and self-association of mono-carboxylic acids by means of low temperature matrix isolation FTIR spectroscopy will be presented.

Multiscale Modeling of Energy Transport for Light-Harvesting and Non-Photochemical Quenching in Higher Plants

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Photosystem II (PSII) light-harvesting complexes (LHCs) are able to collect sunlight and transfer energy to reaction centers with high efficiency through excitation energy transfer (EET). While the photophysics of isolated LHCs has been extensively investigated, their behavior in native assemblies remains poorly understood [1–4]. Recent ultrafast spectroscopy of the M-CP2 subdomain of PSII—comprising LHCII, CP29, and CP24—revealed its EET dynamics, but there is disagreement on how the assembly affects EET compared to isolated complexes [5,6]. These discrepancies highlight the challenge of disentangling overlapping EET processes experimentally.

We employ a multiscale computational approach combining molecular dynamics simulations with quantum mechanics/polarizable molecular mechanics (QM/MMPol) calculations to capture M-CP2's conformational ensemble in membrane [7–9]. To efficiently calculate excitonic parameters for this 67-chlorophyll system, we utilize machine learning models trained on QM/MMPol data, generating thousands of Frenkel exciton Hamiltonians that accurately capture environmental effects [10,11]. Following validation against absorption spectra, we simulate EET dynamics using Redfield–Förster theory [12,13].

By comparing the full M-CP2 assembly with its isolated components, we reveal how supra-molecular organization modulates energy transfer pathways and efficiency, providing mechanistic insights into this key PSII antenna subdomain involved in photoprotection.

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A Unified Framework for Coupled Exciton-Phonon Dynamics using Generalized Nonlinear Exciton Equations

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Accurately modeling the coupled electronic and vibrational dynamics in molecular aggregates is crucial for understanding energy transfer and nonlinear optical phenomena. We present a theoretical framework based on the Nonlinear Exciton Equations (NEE), derived non-perturbatively from the Heisenberg equation of motion for a Frenkel exciton Hamiltonian. A central feature of our model is the introduction of generalized commutation relations for excitonic operators, allowing for a continuous interpolation between pure Bosonic and Paulionic statistics via a single parameter, η. This provides a flexible description of molecular excitations that do not strictly conform to either limit.

The framework is extended to include a harmonic vibrational bath linearly coupled to the electronic system. We systematically derive the hierarchy of equations governing the time evolution of not only the pure excitonic variables (populations and coherences) but also the mixed exciton-phonon correlation functions. A key analysis explores the physical meaning of common approximations. We demonstrate that a full factorization of the exciton-phonon expectation values is equivalent to a mean field model, where quantum excitons interact with a classically treated vibrational bath. This work establishes a rigorous and flexible foundation for simulating complex, non-perturbative vibronic dynamics in molecular systems, providing a pathway to explore phenomena beyond the semiclassical limit. The method is particularly well suited for modeling ultrafast spectroscopy in molecular aggregates, photosynthetic complexes, and other multi-chromophore systems.

Predicting Structure–Function Correlation in Light Harvesting Complexes of Diatoms via Computational Approaches

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Diatoms are unicellular photosynthetic eukaryotic algae that play a fundamental role in marine ecosystems, contributing significantly to global oxygen production and forming the foundation of aquatic food chains. Their ability to survive under diverse and challenging environments, characterized by fluctuating light conditions, depends on a highly adaptable photosynthetic machinery capable of switching between efficient light harvesting (LH) and photoprotective (PP) mechanism. This regulation is primary mediated by fucoxanthin and chlorophyll-*a*/*c* binding proteins (FCPs), the main light-harvesting complexes in diatoms. However, the molecular mechanism that enables these complexes to switch between capturing light energy and dissipating excess energy as heat remains unclear. In this study, we investigate the fundamental structure-function correlation in diatom FCPs, particularly how this relationship enables an intrinsic transition between LH and PP modes. By employing a computational framework that integrates molecular dynamic simulations with Machine learning algorithms, we identified distinct interconverting structural states that are linked to intrinsic transition between light harvesting and photoprotection. Furthermore, we explore the synergistic contribution of the photoprotective protein LHCX1, together with xanthophyll cycle pigments diadinoxanthin (Ddx) and diatoxanthin (Dtx) which are key modulators of these acclimation sates. Our finding provides novel atomic-level insights into the dynamic regulation of photosynthesis in diatoms and lay the foundation for potential bioengineering strategies to enhance light utilization efficiency and stress resilience in these ecological and biotechnologically organisms.

Abstracts of

Poster Presentations

Multiscale Simulation of the Fucoxanthin Chlorophyll *a*/*c* Protein Complex from the Diatom *C. Gracilis*

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Diatoms are a diverse group of algae with an important biological role, producing at least 20% of the oxygen in our atmosphere through photosynthesis. Recently, the crystal structure of *Chaetoceros gracilis* was resolved, making it a valuable model system to investigate light harvesting and energy transfer processes. Particular attention has been given to the fucoxanthin chlorophyll protein (FCP) antenna complexes, which contain pigments such as chlorophyll *a* (Chl *a*) and chlorophyll *c* (Chl *c*). Building on previous studies [1], a multi-scale computational approach has been employed to bridge the classical and quantum perspectives by combining molecular mechanics (MM) simulations with hybrid quantum/molecular mechanics (QM/MM) methods using the computationally efficient Density Functional Tight Binding (DFTB) approach for the ground state dynamics and excited state energy calculations. This framework enables the exploration of the conformational dynamics of the system and the molecular interactions involved in photosynthesis, while also assessing the influence of environmental and structural changes. Furthermore, the effect of pH variation is being investigated, as earlier research [2] has shown that a decreased pH value can significantly impact the role of Chl *c*, resulting in shifts in the energy level landscape within the complex.

Based on these simulations, excited state properties have been analyzed using multi-scale computational methods to predict the excitation energies, excitonic couplings, and spectroscopic features such as spectral densities and absorption spectra, which are compared to experimental results for validation. Additionally, the electric field effect induced on the Chl *c* pigments by the protein environment is being investigated, following previous work [2] that emphasizes its importance in the energy transfer process.

In conclusion, this work aims at deepening our understanding of the quantum mechanical principles that govern photosynthesis and the light harvesting process.

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Elucidating the Exciton Transfer Mechanism in LHCII through Machine Learning

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Understanding excitation energy transfer (EET) mechanism in light-harvesting complexes (LHCs), particularly in light-harvesting complex II (LHC II), is fundamental to explain how photosynthetic systems capture and direct light energy with high efficiency. EET dynamics are determined by site energies, excitonic couplings, and structural rearrangements, all of which require accurate modeling. To describe the coupled electronic and nuclear motions involved in these processes, we use non-adiabatic molecular dynamics (NAMD) combined with the long-range corrected time-dependent density functional tight binding (TD-LC-DFTB) method, within a quantum mechanical/molecular mechanical (QM/MM) framework. However, the computational cost of such simulations is significant, particularly for large systems. To overcome this limitation, we utilize neural network (NN) models trained on TD-LC-DFTB data, allowing for rapid and reliable predictions of site energies, couplings, and forces. By integrating NNs, we aim to accelerate the investigation of EET processes and deepen our understanding of the structural and functional interactions that drive energy transfer in light-harvesting complexes.

Quantum Chemical Comparison of Photosynthetic Special Pairs

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Photosynthetic reaction centers (RCs) are pigment–protein complexes responsible for converting excitation energy from sunlight into chemical potential through ultrafast charge separation and electron transfer. RCs contain centrally positioned tightly coupled pigment dimers known as special pairs (SPs), consisting of two stacked chlorophylls or bacteriochlorophylls. Their coupling enables their unique function in charge separation and determines their optical and redox properties. There is a variety of RCs and SPs in photosynthetic organisms. For example, in oxygenic photosynthesis two photosystems (II and I) operate in series to drive the linear electron flow that powers water oxidation and NADP+ reduction. Each has its own chlorophyll-based SP, known as “P680” and “P700” (the numbers denote absorption maxima), with limited variants of the latter. Anoxygenic photosynthetic bacteria have bacteriochlorophyll-based SPs that include P800 (heliobacteria), P840 (green sulfur bacteria), P870 (green/purple non-sulfur bacteria) and P890 (purple sulfur bacteria), and P960 (Blastochloris viridis). What differentiates photosynthetic SPs is the chemical nature of the two pigments and the precise way they interact, which is primarily affected by their stacking (distance, orientation, and overlap of the macrocycles). Our goal is to provide a detailed quantum chemical comparison of all different photosynthetic special pairs, with particular emphasis on structural, electronic, spectral, and redox properties. To this end, we utilize high-resolution structures to create accurate models for each SP, and probe their ground-state and excited-state electronic structures with quantum chemical methods in order to correlate specific structural parameters with spectroscopic and redox properties. Among others, we explore the applicability of the local energy decomposition (LED) scheme that utilizes domain-based local pair natural orbital coupled cluster calculations, DLPNO-CCSD(T), as a way of obtaining new insight into the nature of the interactions that stabilize the SPs and differentiate their properties.

Molecular Determinants of the Mechanism of Action of PSBS under the Computational Microscope

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Plants require sunlight to survive. However, upon a sudden increase of light intensity, an excess of photoexcitations in the photosynthetic membrane (thylakoid) may cause damage via photooxidation. To avoid this, photosynthetic organisms activate a mechanism called energy dependent quenching (qE) to protect themselves [1].

The sites of this activation are Light Harvesting Complexes (LHCs), membrane protein complexes that bind chlorophylls and carotenoids and are located in the thylakoid membrane [2]. The activation of qE in the LHCs is triggered by the acidification of the thylakoid lumen. As the LHCs are not able to sense the acidification, they require external triggers [3]. In plants the trigger is the pigment-less protein PsbS [4] which is able to sense and respond to changes of pH via conformational changes [6]. However, what is the mechanism of interaction of PsbS with the LHCs? How does PsbS-LHCs interaction activate qE?

We here used a combination of state-of-the-art molecular dynamics methods to study the mechanism of action of PsbS on the LHCs across different levels of resolution. We find that instead of a simple binary switch, PsbS acts with a more nuanced mechanism to fine tune its effects on the membrane and the LHCs.

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Theory of Charge Transfer and Primary Electron Transfer in Open and Closed Reaction Centers of Photosystem II

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Photosystem II (PSII) is the sole biological system known to date that can oxidize water to molecular oxygen via a series of electron transfer (ET) steps. Building on earlier research, the aim of the present work is to gain insight into mechanistic details of primary electron transfer in open and closed PSII reaction centers (RC). It is predicted [1] that the rate of primary electron transfer will be in the range of 1/18 ps for the closed reaction center and 1/300 fs for the open reaction center. The slower transfer rate of the closed reaction center is suggested to lead to the protection of reaction center pigments by allowing the excitation energy to escape into the antenna, thus preventing the formation of harmful triplet states.

Molecular dynamics (MD) simulations of the PSII monomer (PDB ID: 3WU2) were conducted for 150 ns. The snapshots obtained from the MD simulations are employed in the calculation of vertical excitation energies of the ChlD1-PheoD1 dimer via time-dependent density functional theory (TD-DFT) with quantum mechanics/molecular mechanics (QM/MM). A subsequent Multi-FED-FCD diabatization [2] is used to assess the energies of charge transfer (CT) states, local excited (LE) states, and the coupling between them. Marcus' theory is applied to calculate the rate constant for primary electron transfer between the excited ChlD1 and PheoD1.

The results thus far show that the electronic coupling between the LE state and the CT state is essentially constant for all conformers. Furthermore, the CT state energy is strongly dependent on conformations, showing an increase of circa. 4000 cm^{-1} for closed RC which leads to a strong suppression of primary electron transfer. Sub 100 fs time constants are obtained for the primary ET of open reaction centers.

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pKa Prediction for LHC Residues, in the Presence of LHC-Protein and LHC-Carotenoid, Lipid Interactions

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Accurate prediction of pKa in Light-Harvesting Complexes (LHCs) is essential for elucidating their functions in photosynthesis or photoprotection. However, important pKa shifts occur due to the presence of nearby molecules (residues, lipids, pigments or water) and environmental factors (ionic strength) which difficults the quantitative determination of pKa.

From a structural point of view, pKa is the pH at which a titratable residue is observed in a 1:1 ratio between its deprotonated and protonated states. As such, pKa can only be considered as an ensemble average property. Nevertheless, pKa is generally determined without considering the conformational flexibility associated to the switch in the protonation state. To overcome this challenge, we employ constant-pH Molecular Dynamics (CpHMD) simulations, which make use of λ-dynamics performed in a grand canonical ensemble for the titratable protons. With this approach, we explore the conformational landscape at several pH conditions, producing titration curves from which pKa can be extracted.

For this poster presentation, we present our ongoing work toward developing a robust, data-driven model that connects experimental data with structural information derived from CpHMD simulations. In particular, we focus on determining the effect that the local environment has on the pKa shifts of titratable residues. We show how to gain insight by clustering CpHMD trajectories based on interaction types, as given by PDBe-arpeggio. This characterization is versatile, which makes it valuable to future implement in the description of de-novo LHCs protein structures.

Fluorescence-Detected Two-Dimensional Spectroscopy of Exciton Dynamics and Annihilation Using Coarse-Grained Simulations

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A fluorescence-detection approach to two-dimensional electronic spectroscopy (2DES) offers higher sensitivity when compared to traditional techniques. Despite its advantages such as background-free signal, compatibility with microscopy, and single-molecule applications, theoretical modelling is still required to interpret the spectra and draw solid conclusions from Fluorescence-detected two-dimensional spectroscopy (F-2DES) experiments [1]. Widely sought for its ability to study excitation energy transfer in complex molecular assemblies, even the traditional 2DES technique remains computationally challenging for large systems. Recently, a coarse-grained approach to model 2DES [2] was developed aiming to overcome such computational difficulties.

Here, we extend this coarse-grained method, enabling us to investigate the spectroscopic signatures of exciton annihilation events. We performed coarse grained simulations of the F-2DES for the light-harvesting II (LH2) complex of purple bacteria as a broadly tested system. In contrast to coarse-grained simulations of the 2DES for LH2, this new fluorescence-detected simulation technique reveals cross peaks at zero and early waiting times, in accordance with experiments [1].

Parameters like the fluorescence and radiative lifetimes as well as exciton-exciton annihilation (EEA) time can be given as input as taken from literature or used as model parameters. We observe that when setting the EEA rate as zero, we recover the results from regular coarse grained simulation of the 2DES. This indicates that the cross-peaks observed in F-2DES correspond to EEA events, confirming the interpretation put forward previously [3]. New waiting time dynamics studies and application of this F-2DES method to other photosynthetic systems are underway.

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Fourth Order Extension of Exciton Population Transfer Rates

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The excited state energy transfer (EET) is an essential process in photosynthetic systems, optoelectronic devises and many systems investigated with (optical) spectroscopy. Describing the EET in complex open quantum systems is difficult, especially in intermediate parameter regimes. In the limit where the population transfer between molecular aggregates is incoherent, one can make use of the recently implemented Time Domain Förster Resonant Energy Transfer [1,2] (TD-MCFRET) method to determine the population transfer rates between the aggregates. In this work we present a fourth order perturbation theory that extends the TD-MCFRET method and allows for the more precise calculation of population transfer rates between molecular aggregates in intermediate regimes of coupling and system memory. The fourth order correction can also be used to improve the accuracy of FRET models. We present a computationally tractable way of determining these higher order corrections and demonstrate their relevance and validity for a set of realistic systems. This new theoretical refinement may improve the interpretation of various experimental techniques such as absorption, fluorescence and 2DES spectroscopies and will deepen our understanding of EET in photosynthetic systems, synthetic devises and beyond.

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Protonation State and Structural Control of Exciton Transfer in Cryptophytes

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Cryptophytes are unicellular algae found in diverse aquatic environments, capable of capturing sunlight underwater and transferring energy via tunable straight-chain tetrapyrrole chromophores known as bilins. Their unique phycobiliproteins exhibit strong photosynthetic activity under low-light conditions, which has attracted significant interest in revealing their electronic energy transfer mechanisms. In this study, we employed multiscale simulations using a computationally efficient density functional tight-binding framework to investigate the energy transfer processes in the PC645 and PC612 complexes, which correspond to the so-called closed and open forms, respectively. The insertion of a single aspartic acid residue in the protein induces an approximately 73-degree rotation of the monomer, creating a cavity at the center of the complex. This conformational difference significantly influences the electronic interactions between the central pigments and the spectral properties of the system. More interestingly, the protonation states of certain bilins in the closed form complex remain uncertain, and our results demonstrate a mechanism to modulate the excitation energies, excitonic couplings, and intra-molecular vibrational modes with different protonation states. As a result, the exciton transfer rates change, leading to different energy transfer pathways within the complex.

Shedding Light on the Excited State Dynamics of DNA-Templated Silver Nanoclusters

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DNA-templated silver nanoclusters (DNA-AgNCs) are fluorescent nanomaterials of small silver clusters (8–30 atoms) stabilized and templated by short DNA strands. DNA-AgNCs exhibit unique optical properties, including strong absorption, efficient emission with broad spectral bands (even in the near-IR), and large Stokes shifts [1,2]. These features are broadly tunable by the change in DNA sequence, making them promising for diverse biosensing applications. However, the exact role of DNA in influencing the excited-state energy landscape and its site-selective binding to metal clusters, which leads to ultra-fast relaxation processes and a very high fluorescence quantum yield, remains largely unexplored.

In this study, we investigate a DNA-AgNC composed of three single-stranded DNA sequences and 21 silver atoms with a total charge of +15 (DNA_3-Ag_{21}NC) [3], using two-dimensional electronic spectroscopy (2DES). At room temperature, the system exhibits a notably high fluorescence quantum yield of 73% with an emission maximum at 721 nm. We observe a continuous relaxation of the stimulated emission within <100 fs, spanning the complete Stokes shift and extending slightly beyond, followed by a slight blue shift over the next ~300 fs. This unusual dynamic behavior raises questions about the involvement of structural changes and wave packet motion in the excited state. Additionally, coherent beat analysis reveals multiple low-frequency vibrational modes around 100 cm^{-1}, not reported in previously measured DNA-AgNCs [4].

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Generalized Description of Non-Adiabatic Dissipative Energy Dynamics in Porphyrin Derivatives

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Theoretical spectroscopic models involving diabatic coupling between excited electronic states have proven to be successful in describing the static and time-resolved optical spectra of porphyrin molecule derivatives—notably of various chlorophylls which have a vital role in pigment–protein complexes of the majority of photosynthetic organisms. The current modeling approach is based on the addition of selected vibrational modes that facilitate the diabatic coupling into the system Hamiltonian. However, this approach has severe scaling limitations. The system Hamiltonian of a single molecule increases exponentially in size with the number of vibrational modes added and linearly with the number of vibrational levels included, i.e. the extent of truncation. Propagating such a model in time and optimizing its physical parameters to fit the experimental data is a challenging task even in the case of a single molecule. Large molecular complexes composed of dozens of molecules become intractable.

We propose a new approach to alleviate this limitation by returning the diabatically coupling modes to the thermodynamic bath and performing normal mode analysis on them introducing new effective spectral densities. This procedure substantially reduces the system Hamiltonian size while preserving all non-adiabatic effects present in the original model. Besides, it also lowers the overall coupling strength between the system and the bath rendering perturbative approaches—like the Redfield theory that operates in the limit of weak system-bath coupling—more appropriate.

On a variety of physical systems, we compare the new approach with the one that explicitly includes vibrational modes in the system Hamiltonian. We investigate its validity in a broad range of physical parameters such as diabatic coupling strength, number of vibrational modes, energy gap sizes, and system–bath interaction strengths. In the long run, the new model should enable us to study the dynamical properties of large molecular complexes in greater detail and shed light on the role of non-adiabatic effects in photosynthetic complexes as well as in other systems.

Influence of the Energetic Landscape on Multi-Exciton Energy Transfer and Annihilation

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Excitation Energy Transfer (EET) in photosynthetic complexes and organic solar cells is typically rationalized within a single-exciton picture, in which energy is transferred between the lowest-excited states of individual chromophores. However, at high photon fluences, multiple excitons can be simultaneously generated, whose encounter may result in the net loss of an exciton through a process known as Exciton–Exciton Annihilation (EEA).

Multi-exciton EET and EEA processes are commonly described using phenomenological models which are limited by several underlying assumptions [1,2], e.g., normal exciton diffusion, uniform random distribution, and instantaneous EEA within the so-called annihilation radius. Instead, recent advances in ultrafast nonlinear optical spectroscopy have revealed that exciton diffusion is anomalous rather than normal [3], annihilation can be suppressed by quantum interference [4], and excitons can meet several times before eventually annihilating [5]. Although some microscopic theories have been proposed [6-8], a comprehensive understanding of multi-exciton EET and EEA processes is still lacking.

To fill this gap, we developed a multi-exciton description of EET and EEA in molecular systems by extending the Frenkel exciton model to explicitly include higher-excited states of each chromophore. Focusing on molecular chains with a varying number of sites, we investigate how static disorder, many-body interactions, energy mismatch and excitonic coupling act in shaping the energetic landscape of the manifold. Depending on the degree of delocalization between two-exciton and higher-excited states, we employ three different microscopic theories, i.e., Förster, Redfield, and combined Förster–Redfield theories, to determine under which conditions EEA rates are enhanced or suppressed.

Our findings will provide the foundation for interpreting spectral features observed in higher-order optical responses and for establishing novel design principles for improving photovoltaic efficiency.

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Interfacing X-ray Diffraction (XRD) and Molecular Dynamics Modeling for Amorphous Molecular Systems

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X-ray diffraction (XRD) is a powerful analytical technique widely used in material science and crystallography to study the structural properties of crystalline materials [1]. Modeling of XRD spectra of materials, followed by comparison with experimental data, provides valuable insights into their potential applications in advanced technologies and offers a deeper understanding of the arrangement within crystals. Molecular systems are often amorphous, and the molecular organization at finite temperature can be tackled by using molecular dynamics simulations. This study focuses on the development of a computational algorithm designed to calculate the XRD spectra of amorphous materials based on the atomic arrangement within their structures. For this objective, the research utilized the knowledge of numerical and analytical orientational averaging methods and used the Von Laue diffraction formalism to calculate the orientation-averaged intensity distribution of the diffracted radiation for the selected nanocrystals. Calculations of XRD from molecular dynamics simulations and direct comparison to XRD experiments allow direct inspection of molecular organization within molecular systems.

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Complete Exciton Hamiltonian for Photosynthetic Pigment–Protein Complexes

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One of the core processes of photosynthesis is the “collection of the light energy” through excitations of multi-pigment light-harvesting antenna complexes. A vast diversity of photosynthetic pigments and light-harvesting complexes has evolved, what adapted the process to occur both in water and on land, and it can be found in many bacteria, algae, and plant species. In this work, we extend the standard exciton model typically used to calculate various types of spectra of the light-harvesting complexes. The standard exciton theory used for describing the spectroscopy of molecular complexes usually assumes an infinite exciton lifetime, coming from complete isolation of Hamiltonian blocks describing a different number of excitations. We focus on extending the model by including environment-induced non-resonant couplings in the Hamiltonian, which couple different numbers of excitons. We analyze their impact on the absorption spectra of two small light-harvesting complexes from their crystallographic structure: Fenna–Matthews–Olson and fucoxanthin–chlorophyll protein. Quantum mechanics calculations of the pigment properties, combined with electrostatic description of the protein, allowed us to construct the full Hamiltonian and calculate the exciton lifetimes and the absorption spectra using the secular Redfield theory. The results of the research indicated that off-resonant terms in the Hamiltonian are significant and should be included in the calculations of linear (or non-linear) spectra. Therefore, as the results proved to be significant, the methodology of this model was advanced: molecular dynamics simulations have been performed for the protein and its ligands to get closer to the real-life conditions than the single crystallographic structure. The molecular dynamics simulations allowed us to obtain correlation functions and spectral densities of the Fenna–Matthews–Olson complex with the off-resonant terms and to focus on developing the complex Redfield theory extension including the off-resonant terms for absorption calculations.

Using Transformer Neural Networks to Speed up Molecular Structure Optimization at DFT Level

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Transformer neural networks are a relatively recent innovation in machine learning [1], which have enabled the development of the now widely popular large language models (ChatGPT, LlaMA, etc.) and achieved excellent results in translation and image generation tasks. With certain modifications, this architecture has also proven highly effective in predicting protein structures from amino acid sequences [2]. The main strength of transformer NNs lies in encoding data into descriptive numerical vectors and the attention mechanism, which allows the model to recognize even very subtle correlations within the data. This type of network is particularly well suited for modeling one-dimensional, i.e., sequential, systems. On the other hand, their effective application to data in higher-dimensional spaces remains an actively investigated question. Molecular structures are usually optimized in three-dimensional space, thus applying this architecture efficiently to model molecular structure is a non-trivial task. Various neural networks are already used in quantum chemistry calculations and allow optimization of molecular structures, as well as calculation of forces and dipole moments, on personal hardware much faster than performing density functional theory (DFT) calculations on supercomputer nodes [3, 4]. The main drawbacks of neural network–based methods compared to DFT are empirically derived energy values not grounded in the variational principle, the "black-box" effect, and relatively poor generalization to molecular compounds not present in the training dataset.

In this study, using the transformer neural network architecture, we aim to evaluate whether it is possible to obtain DFT-accuracy molecular structures in the ground state, while requiring only a fraction of the usual computational resources for new structure calculations, by leveraging existing datasets of quantum mechanical calculation results. As a starting point, we selected an open-access dataset [4] containing about 3.9 million molecular structures optimized using the B3LYP 6-31G(d) DFT method. From this dataset, we removed monoatomic and non-interacting diatomic systems, generated SMILES and SELFIES descriptors of these molecules, and determined their point symmetry groups using the SOFI [5] algorithm with certain modifications. We also trained a transformer neural network on these data to predict molecular point symmetry groups and other geometric properties, such as planarity and mirror symmetry.

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