<div align="center">**PhD proposal, Top Master Nanoscience**</div>

1. Title of research proposal

Electronic excitation energy transport in self-assembled molecular nanotubes.

2. Summary of research proposal

This proposal concerns the study of electronic excitation energy transport in self-assembled molecular nanotubes, particularly the double-walled tubular aggregates of the cyanine dye C8S3[1]. These nanotubes are inspired on tubular chlorophyll aggregates that occur as extraordinary efficient light-harvesting systems in nature. Tubular aggregates have a wire-like structure with a robustness against disorder through a second rolling dimension. Because of their hierarchical structure, these aggregates experience energy transport taking place at different scales. The aim of this research is to study their dynamics by implementing the time-dependent exciton Hamiltonian into a combination of the Numerical Integration of the Schrödinger Equation (NISE) method and the surface hopping method. This method allows for the calculation of 2D spectra which will elucidate the dynamics of the system. The dependency on temperature and the effect of incorporating modified molecules (traps and launchers) will be investigated. To compare the model with real experiments, one has to average over many model realizations. Because these aggregates might consist of thousands of molecules, this approach will be very challenging but realistic, particularly if the noise is translated into a bath consisting of Brownian oscillators.

3. Applicant

G. J. J. Lof

4. Key publications of the applicant

N/A

5. FOM-research group

B-13

6. Institute

Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4

University of Groningen
Zernike Institute
for Advanced Materials

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[1] 3,3'-bis(2-sulphopropyl)-5,5',6,6'tetrachloro-1,1' dioctylbenzimidacarbocyanine

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7.   Duration of the project

Four years: starting at April 1st, 2014 and continuing until April 1st, 2018.

8.   Personnel

8.1. Senior-scientists

name	main tasks
prof. dr. J. Knoester *Theory of Condensed Matter (RUG)*	supervision PhD student project management
dr. T. l. C. Jansen *Theory of Condensed Matter (RUG)*	supervision PhD student project management

8.2. Junior-scientists

name	main tasks
PhD student (G. J. J. Lof) *Theory of Condensed Matter (RUG)*	research

9.   Costs

9.1. Personnel positions

One PhD position for four years (204 k€)

9.2. Running budget

Exploitation cost: 20 k€ (i.e. 5 k€ per year)

9.3. Equipment

- Desktop or laptop for the PhD student (2 k€)
- Reasonable contribution to the local computer-cluster of the Theory for Condensed Matter group (15 k€)

9.4. Other support

The University of Groningen will support the project in the positions of senior-scientists prof. dr. J. Knoester and dr. T. l. C. Jansen.

9.5. Budget summary

The funding is requested for one PhD position (four years).

	2014	**2015**	**2016**	**2017**	**2018**	**total**
personnel positions	0.75	1	1	1	0.25	4
personnel (costs)	38.25 k€	51 k€	51 k€	51 k€	12.75 k€	204 k€
running budget	3.75 k€	5 k€	5 k€	5 k€	1.25 k€	20 k€
posting	-	1 k€	1 k€	1 k€	1 k€	4 k€
equipment	17 k€	-	-	-	-	17 k€
total	59 k€	57 k€	57 k€	57 k€	15 k€	**245** k€

10. Research programme

10.1. Introduction

In 1937, Jelley [1] and Scheibe [2] discovered some remarkable properties of dye molecules. They observed that the optical properties of the dye pseudo-isocyanine (PIC) strongly depend on its concentration in aqueous solution. With increasing concentration the band of maximum absorption was both found to shift to lower energies and to become much narrower. Aggregates that exhibit such a red-shifted absorption band with respect to the monomer absorption peak are nowadays known as J- or S-aggregates. Jelley and Scheibe attributed this phenomenon to clustering of the molecules into large aggregates. Aggregates exhibiting a blue-shift with respect to the monomer absorption peak do exist as well, which are known as H-aggregates. Whether an aggregate is of the J- or H-type, depends on the relative orientation of the transition dipoles of the monomers. The shift and narrowing of the absorption peak can be understood in terms of collective excitations, known as Frenkel excitons. These excited state wavefunctions are delocalized over several monomers within the aggregate due to coherent coupling of the transition dipoles.

An important application for aggregates is as sensitizers in silver halide photographic films, in particular cyanine dyes [3]. Recently, it was discovered that the light-harvesting systems of photosynthetic bacteria and higher plants consist of self-assembled aggregates [4],[5]. In many of these natural systems, incredibly large internal quantum efficiencies are reached, as high as 95%, which is the ratio of the number of free charges in the photosynthetic reaction centre and the number of primary photoexcitations. Fundamental understanding of the success of these natural systems in terms of the dynamics of the energy transport might promote the development of artificial light-harvesting systems [6] and, more generally, efficient molecular energy transport systems like nanowires.

Chromophores might even contribute to the development of quantum-computers, which is studied in the upcoming field of quantum biology [7].

Nowadays, many systems are known where dye molecules self-assemble into molecular aggregates via non-covalent interactions like π-stacking, Van der Waals interactions, and hydrophobicity/-philicity [8],[9]. Such molecular self-assembly is believed to be a promising bottom-up approach to build nanoscale functional materials. By manipulation of the circumstances under which the self-assembly occurs, such as the structure of the monomer, the solvent, the temperature or external forces, it is possible to influence the formation of the end product. Tubular aggregates are particularly interesting because of their wire-like structure together with their robustness against disorder through the second rolling dimension. Several systems consisting of tubular aggregates have been created in the past decade [10],[11],[12], with typically diameters of about 10 nm and lengths in the order of microns. Interestingly, tubular aggregates occur in nature as chlorosomes in the Green Sulphur bacteria, which is one of the most efficient light-harvesting systems known [13],[14].

In this project, the focus will be on aggregates of the dye C8S3 that form in solution (Fig. 1). Cryo-EM reveals a hierarchy of self-assembled structures including double-walled nanotubes and under certain conditions bundles of nanotubes [15]. Hence, this system allows for the occurrence of electronic excitation energy transport at various levels; within one wall, between walls of one tube, and between different tubes.
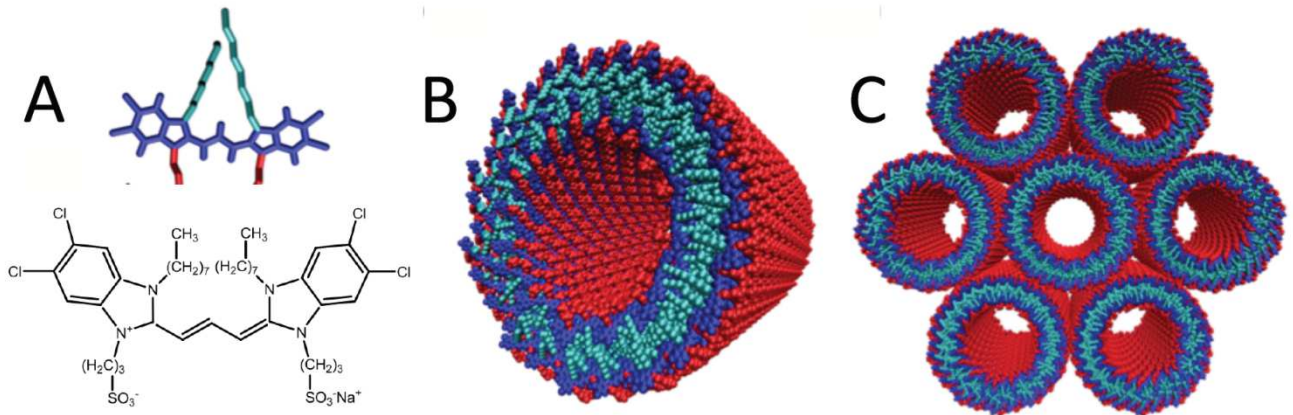

Figure 1: The hierarchical structure of C8S3 aggregates [16]. (A) Single C8S3 molecule. (B) Double-walled tube. (C) Bundle of seven double-walled tubes. Chromophores are depicted in dark blue, hydrophilic groups in red and hydrophobic hydrocarbon tails in light blue.

10.2. State-of-the-art

The optical response of the C8S3 double-walled cylindrical aggregates is relatively well-understood by now. The experimentally obtained linear absorption spectra can be explained in terms of models in which the optical response of both walls is superimposed, without allowing electronic coupling between the walls [16],[17],[18]. However, it is not so well-understood why for example the walls should be seen as uncoupled, as model calcu-

lations have shown the possibility of exciton coherence within the entire double-walled aggregate when all resonant transfer interactions are taken into account [19]. Possibly, the presence of a dynamical environment can explain this. The dynamic disorder caused by e.g. intermolecular vibrations and phonons in the solvent might well be of the same order as the resonant transfer interactions between the two walls, thereby destroying the coherence. In other research fields it has already been shown that vibrations can significantly alter the optical properties of a molecular system [20],[21]. To correctly account for the environment in the models, is one of the main challenges of this project.

Several numerical methods have been developed that treat the environment stochastically. An example that has been applied to double-walled cylindrical aggregates is Redfield theory [22], which is a perturbative method that uses Pauli's Master Equation. Within this approach, the quantum system has its energy levels on average separated by an energy difference ΔE. Additionally, a perturbation σ is applied to the energy levels. From the rate equations one obtains a rate k, i.e. the probability for a transition to occur per unit of time, with k being proportional to the inverse of ΔE. Hence, in order to describe a system perturbatively, ΔE should be large enough. Usually, when ΔE is in the order of σ, the rates are not reliable anymore. Because large aggregates have many energy levels, the energy difference ΔE becomes very small. When this approach is applied to large aggregates one might therefore doubt whether k is still reliable.

Other examples that treat the environment stochastically are cumulant expansions [23], and stochastic Schrödinger and Liouville equations [24],[25]. The downside that all these methods have in common is their dependence on phenomenological spectral densities, and that they provide little insight in the correlation between the chromophores and the environment.

In that respect, an attractive alternative is to use quantum-classical dynamics, which allows for an explicit parametrization of the environment through classical coordinates. A notable example of this approach is the Numerical Integration of the Schrödinger Equation (NISE) method [26],[27]. This method models the classical environment as Brownian oscillators [28], or through more elaborate molecular dynamics simulations [29]. NISE is a relatively inexpensive method which has proven to be very effective as a basis for simulating 2D infrared spectra, particularly for polypeptides [30]. However, implementations of NISE conventionally treat the quantum-classical interaction inconsistently, by neglecting the feedback of the quantum system on the classical coordinates. This implies that NISE is an infinite-temperature approach, which is too restrictive for most spectroscopies in the visible regime, particularly for modelling temperature dependent quantities.

A straightforward approach is to calculate this quantum feedback according to Ehrenfest's theorem [31], by using the weighted average of the quantum energy potential. However, this method leads to incorrect thermalization and is unable to properly describe the branching of quantum states. To meet this drawback, several so-called surface hop-

ping approaches have been introduced which aim to incorporate the classical reaction to the quantum branching phenomenon. A notable example is Tully's fewest-switches surface hopping (FSSH) procedure [32], which is able to induce a relaxation of the quantum populations towards a Boltzmann distribution [33],[34]. NISE has successfully been complemented with FSSH for a dimer system [35]. Implementing and using this approach for large systems, consisting of a few thousand molecules, will be challenging but realistic, in particular if the noise is translated into a bath consisting of Brownian oscillators [23].

10.3. Motivation and innovative aspects of the proposed research

Studying the electronic excitation transport experimentally is a challenging task mainly because of the fact that due to the diffraction limit it is hard to define with sufficient accuracy a start and an end point for optical excitations between which the transport is observed and may be characterized. A novel experimental technique to study the dynamics of electronic excitations is 2D spectroscopy [36]. This technique allows to extract molecular information like optical transition frequencies, dipole moment orientations and mutual couplings. For the interpretation of 2D spectra, theoretical knowledge and simulations are required. In this research it is aimed to model 2D spectroscopy to study the dynamics of double-walled C8S3 aggregates. These model results will be compared to experiments to be performed in the group *Optical Condensed Matter Physics* (Pchenitchnikov, RUG).

It is challenging to model excitation energy transport in systems that consist of thousands of molecules. Firstly, this is because the transport is the result of a complex interplay of the interactions within the aggregate and with its surroundings. Secondly, because of the diffraction limit, it is hard to resolve the molecular packing in these aggregates. Consequently, molecular structures applied thus far to models have been constructed in a phenomenological way [16].

In this respect, molecular dynamics (MD) is considered to be an appropriate tool to simulate atomistic scale equilibrium structures. However, MD has not yet been applied to simulate the structure of large assemblies of dye aggregates. Generating proper force fields and achieving equilibration in such large systems will be very challenging. These MD calculations will be provided by the *Molecular Dynamics* group (Marrink and de Vries, RUG). With the aid of quantum chemical techniques, the MD information is then translated into a time-dependent Hamiltonian for the excitations of interest. Using quantum statistical methods, this will be used to model the excitation energy dynamics, as well as various optical spectra.

The use of MD will provide a more fundamental understanding of the molecular packing and the excitation energy transport in molecular aggregates. Also, this approach is to be expected to be much more accurate than the use of a phenomenologically constructed Hamiltonian. However, the models that will be used to study the dynamics do not prin-

cipally depend on input from MD. This enables to use the phenomenological approach as a backup plan.

10.4. Goals of the proposed research

- Taking the environment of self-assembled nanotubes into account in simulations
- Studying the dynamics by comparing theory and experiments
  - To what extent is the transport coherent?
  - Is it possible to control the degree of coherence, for example by varying the temperature?
  - What is the transport length and direction?
- Studying the effect of traps and launchers
- Formulation of design rules for optimal transport properties

10.5. Background

Already in the 1930's, Frenkel [37] and Peierls [38] suggested the existence of collective electronic excitations. The general concept is introduced most easily by approximating a molecule by a two-level system [39], consisting of a ground state and an optically dominant excited state. When N molecules are decoupled, there will be an N-fold degenerate lowest excited state, corresponding to one molecule being in the excited state. This is referred to as a molecular exciton, where the electron and hole are located on the same molecule. Interactions between different molecules break the degeneracy which induces the exciton wavefunction to delocalize. Such a shared excitation is known as a Frenkel exciton. In molecular systems, these interactions are mediated by the optical transition dipoles of the molecules. The new eigenstates correspond to excitations that are coherently shared by several molecules. This delocalized nature of the electronic excitations has important consequences for the optical and transport properties, as the system will collectively interact with incoming light or its surroundings.

Generally, it is important as well to take the interactions with the environment into account. Due to inhomogeneities, the excitation energies and couplings will vary from molecule to molecule. Such disorder leads to localization of the Frenkel excitons, where the wavefunctions are no longer extended over the entire molecular system, but only over a region called the localization length.

Quantum-classical dynamics studies the interaction between a quantum system and the environment via a system-bath separation [35],[40]. Often, the quantum system is assumed to consist of an assembly of interacting two-state quantum units. The bath can then be represented by coupling each quantum unit linearly to a classical coordinate, as shown in Fig. 2.
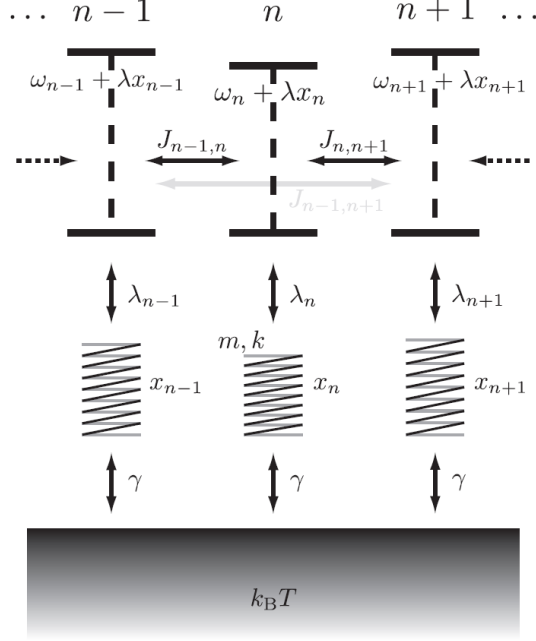
Figure 2: Schematic illustration of a quantum-classical system [35].

Each two-state unit is attributed a site index n, and a transition energy ω_n. The influence of the bath on the quantum system is taken into account by coupling site n to bath coordinate x_n which is manifested as a change of the transition energy ω_n by an amount of $\lambda_n x_n$, where λ_n is the coupling parameter. Interaction between sites n and m, denoted $J_{n,m}$, results in a delocalization of quantum excitations. The exciton Hamiltonian becomes

$$H = \sum_n (\omega_n + \lambda_n x_n) B_n^\dagger B_n + \sum_{n,m} J_{n,m} B_n^\dagger B_m \,,$$

where $B_n^{(\dagger)}$ annihilates (creates) an excitation at site n. Note that $\hbar = 1$ is taken, and that the ground state is associated with the zero point energy. Since the classical coordinates x_n are changing in time, the exciton Hamiltonian together with its eigenstates $\left| \varphi_k \right\rangle$ and eigenenergies ε_k are parametrically time-dependent. At every instant, the state of the quantum system can be expressed as an expansion of adiabatic eigenfunctions,

$$\left| \Psi \right\rangle = \sum_k c_k \left| \varphi_k \right\rangle,$$

with its evolution being determined by the time-dependent Schrödinger equation

$$\left| \frac{d\Psi}{dt} \right\rangle = -iH \left| \Psi \right\rangle.$$

Within the NISE method the Hamiltonian H is assumed to be constant during a small time interval Δt, over which the wavefunction propagates as

$$\left| \Psi(t + \Delta t) \right\rangle = e^{-iH\Delta t} \left| \Psi(t) \right\rangle.$$

The bath coordinates are described by classical trajectories directed by the total of acting forces. Following the Brownian oscillator model [23], the situation of damped harmonic motion is complemented with a random fluctuating force to represent the effect of temperature stochastically. The classical dynamics are governed by the Langevin equation

$$m\ddot{\vec{x}} = -k\vec{x} - m\gamma\dot{\vec{x}} + \vec{F}^T + \vec{F}^Q ,$$

where each coordinate x_n is associated with a mass m which performs a damped oscillation with friction and spring constants γ and k respectively. The thermal contribution is represented by the white random force $\vec{F}^T$. The quantum force $\vec{F}^Q$ represents the influence of the quantum system on the classical bath.

Surface hopping, as introduced by Tully and Preston [41], is based on the idea that the classical bath coordinates x_n always evolve on a single potential energy surface. When they evolve on the adiabat ε_k, the state $\left|\varphi_k\right\rangle$ is said to act as an auxiliary wavefunction in providing quantum feedback. The quantum force then takes on the form

$$\vec{F}^Q = -\left\langle\varphi_k\left|\nabla_{\vec{x}}H\right|\varphi_k\right\rangle .$$

Nonadiabatic coupling now affects the classical dynamics through an instantaneous hopping of the auxiliary wavefunction between adiabats (Fig. 3). Tully proposed a fewest switches surface hopping (FSSH) algorithm [32], which allows such a state transition to happen anywhere along the potential energy trajectories provided that the nonadiabatic coupling is nonvanishing. At each instant of time, a random number is drawn to determine whether a hop takes place. In case of a hop, the energy difference is translated into an increase of the kinetic energy of the classical coordinates if the new state has a lower energy. If the new state has a higher energy, the energy difference is taken out of the classical system. If there is not enough classical energy available, the hop does not take place. Such forbidden hops induce a correct thermalization of the quantum populations as derived from the auxiliary wavefunction.
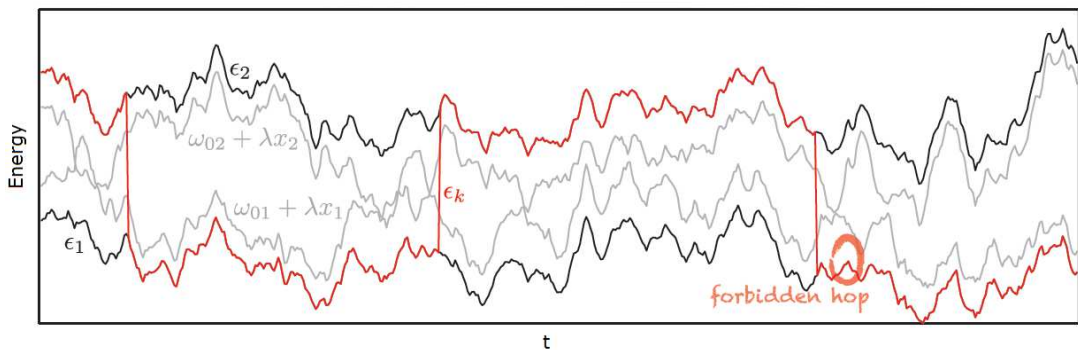

Figure 3: Illustration of the hopping process of the auxiliary wavefunction between two adiabats. Image courtesy of R. Tempelaar.

Two dimensional spectroscopy is an extraordinary useful experimental tool to study energy transfer mechanisms in solids and liquids [36]. It requires four light pulses interacting

with the quantum system. These interactions can be described in terms of six Liouville pathways, which describe the evolution of the part of the density operator that contributes to the optical response. These pathways are called ground state bleach (GB), stimulated emission (SE), and excited state absorption (EA), with each having both a rephasing and nonrephasing variant. The corresponding Feynman diagrams are shown in Fig. 4. Between two consecutive interactions there is a waiting time $t_1/t_2/t_3$ respectively. One scans over t_1 and t_3, while keeping t_2 constant, and then takes the Fourier transform to obtain the signal dependence on the corresponding frequencies ω_1 and ω_3. Taking together multiple 2D spectra for different t_2 provides a movie giving information about the energy transfer after the initial excitation.
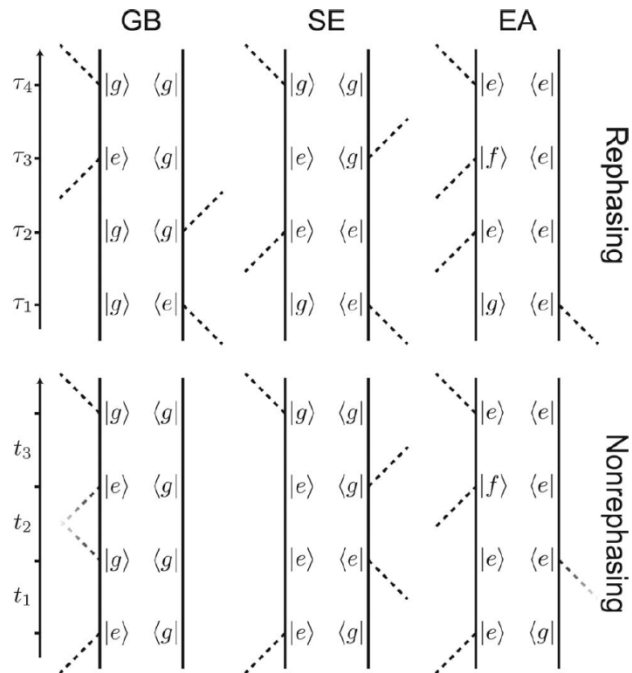

Figure 4: Double sided Feynman diagrams illustrating the six Liouville pathways contributing to the 2D optical signal. Shown are the diagrams for ground state bleach (GB), stimulated emission (SE), and excited state absorption (EA).

The interaction of light with the quantum system is described by the Hamiltonian

$$H_{\text{int}}(t) = \sum_n \vec{\mu}_n \cdot \vec{E}(t)(B_n^\dagger + B_n),$$

where $\vec{\mu}_n$ are the molecular transition dipoles, and $\vec{E}$ the electric field. The NISE/FSSH approach of Tempelaar e.a. to calculate the nonlinear optical response is based on decomposing the contributing Liouville pathways in the adiabatic basis, while branching the classical coordinates in replicas [35]. Only the replicas interacting with quantum populations experience a feedback force, which means that for these cases a fully self-consistent treatment of quantum-classical interaction is realized. This method has been successfully applied to a dimer system.

10.6. Methodology

If MD can be applied successfully to C8S3 aggregates, MD snapshots will provide the atomic scale coordinates of all dye and solvent molecules at small time-steps. These MD data will be used in combination with quantum-chemistry methods to generate the transition energies, transition dipole moments, and intermolecular transfer interactions. The first two will be calculated via a semi-empirical method (ZINDO/S) [42], offering a good accuracy at low computational cost [43]. The latter will be calculated by the TrEsp method (transition charges from electrostatic potential) [44]. This approach allows for the first-principles modelling of the magnitude of the disorder in the transition energies and the intermolecular transfer interactions, as well as its temporal and spatial correlations within the aggregate. These can be used to calculate an average homogeneous Hamiltonian from which optical characteristics can be obtained, such as the absorption spectrum. In this limit, only coherent transport is possible.

By using MD traces instead of snapshots, it is even possible to determine the full time-dependent Hamiltonian. This allows to evaluate (nonlinear) spectra and energy transport properties. This will be performed by using the surface hopping method in combination with NISE.

Determining whether the excited state dynamics and optical spectra are calculated successfully, should be defined by experimental results, particularly 2D spectra. One should note however, that in an experiment one will usually use a sample consisting of many aggregates, while in the model only one aggregate is considered at a time. In order to represent a real experiment, one should thus average over many realizations of the model. Such a procedure is computationally very costly, especially if one would use MD traces for each realization. More appropriate is to use quantum-classical dynamics instead, which is computationally much cheaper, because the environment is modelled by using a Brownian oscillator model. Still, it is recommended to use MD as a benchmark to determine the optimal parameters of the Brownian oscillator model. The use of quantum-classical dynamics is only justified if it provides comparable statistics as MD. In this regard, it is convenient to optimize the Brownian oscillator model until a similar auto-correlation function is obtained.

Once the molecular system together with its dynamics can be modelled correctly, the dependence on temperature, and the influence on traps and launchers will be investigated. The temperature can be varied in the MD simulation, while leaving other parameters unaffected. Exciton traps and launchers can be modelled most easily by varying the diagonal elements of the exciton Hamiltonian. A trap is implemented by a decrease of the chromophore's transition energy, a launcher by an increase (Fig. 5). It will be studied how these implementations affect the structure and time-dependence of the spectra. The model results will be compared to analogous experiments obtained with 2D spectroscopy.
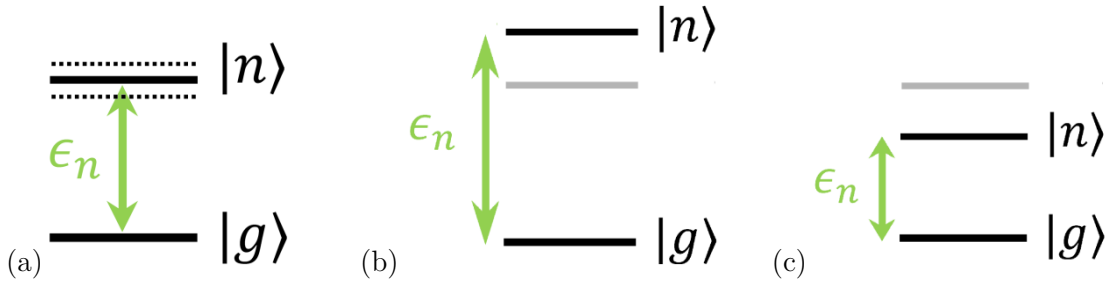
ϵ_n $|n\rangle$ $|g\rangle$ (a) ϵ_n $|n\rangle$ $|g\rangle$ (b) ϵ_n $|n\rangle$ $|g\rangle$ (c)

Figure 5: (a) An illustration of the ground state and excited state of a typical chromophore. Even in an aggregate consisting of equivalent chromophores, the excited state energies are affected by disorder due to the environment, i.e. their excited state energy lies somewhere between the dashed lines. (b) A launcher is a different chromophore with a much larger excited state energy. (c) A trap is a different chromophore with a much smaller excited state energy.

These simulations will provide information about the extent of the exciton states, their transport length and direction, and coherent versus incoherent nature of the transport. Moreover, they may lead to predictions of what favours these properties and what are their optimal optical probes. Also, using the fact that both walls have their own set of dominant exciton transition energies, the dynamics of the various cross-peaks occurring between these transitions in the 2D spectrum provides information about coherence and population exchange between both walls.

10.7. Detailed work plan

The timing of activities are schematically depicted in the following table.

fist year	second year
- literature study - get acquainted with programming in C/C++ - perform QM calculations to support MD - obtain time-independent Hamiltonian from MD snapshots (if MD fails, from phenomenological approach) - calculate linear absorption spectrum - compare to experiments - get acquainted with NISE/surface hopping	- obtain time-dependent Hamiltonian from MD traces (if MD fails, from phenomenological approach) - apply NISE/surface hopping - calculate (2D) spectra and excited state dynamics - compare to experiments
third year	**fourth year**
- investigate the dependence on temperature - investigate the dependence on traps - compare to experiments	- investigate the dependence on launchers - compare to experiments - formulate design rules for optimal transport properties - thesis writing

11. Application perspective in industry, other disciplines or society

The approaches and results of this project will be relevant outside the scope of the involved groups as well. Particularly, they are relevant to the field of organic (opto)electronics, such as for organic photovoltaics where energy transport in complex soft matter is a key issue as well, and to the general bottom-up design of complex hierarchical structures.

12. FOM subfield classification

NANO

13. References

[1] E. E. Jelley, *Nature*, vol. 139, p. 631, 1937.

[2] G. Scheibe, *Angew. Chem.*, vol. 50, p. 212, 1937.

[3] T. Tani, *Oxford University Press:* Oxford, 1995.

[4] H. van Amerongen, L. Valkunas, and R. van Grondelle, *Photosynthetic Excitons, World Scientific, Singapore*, 2000.

[5] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. van Grondelle, *Nature Chemistry*, vol. 3, p. 763, 2011.

[6] M. R. Wasielewski, *Acc. Chem. Res.*, vol. 42, p. 1910, 2009.

[7] M. Sarovar, A. Ishizaki, G. R. Fleming, and K. B. Whaley, *Nature Physics*, vol. 6, p. 462, 2010.

[8] B. Whitesides and G. M. Grzybowski, *Science*, vol. 295, p. 2418, 2002.

[9] S. Zhang, *Nature Biotech.*, vol. 21, p. 1171, 2003.

[10] S. Kirstein and S. Dähne, *Int. J. of Photoenergy*, vol. 2006, no. 20363, 2006.

[11] F. Würthner, T. E. Kaiser, and C. R. Saha-Möller, *Angew. Chem.*, vol. 50, p. 3376, 2011.

[12] V. Gulbinas, R. Karpicz, R. Augulis, and R. Rotomskis, *Chem. Phys.*, vol. 332, p. 255, 2007.

[13] S. Ganapathy, G. T. Oostergetel, P. K. Wawrzyniak, M. Reus, A. G. M. Chew, F. Buda, E. J. Boekema, D. A. Bryant, A. R. Holzwarth, and H. J. M. de Groot, *Proc. Natl. Acad. Sci. U.S.A.*, vol. 106, p. 8525, 2009.

[14] J. Psencik, A. M. Collins, L. Liljeroos, M. Torkkeli, P. Laurinmäki, H. M. Ansink, T. P. Ikonen, R. E. Serimaa, R. E. Blankenship, R. Tuma, and S. J. Butcher, *J. Bacteriol.*, vol. 191, p. 6701, 2009.

[15] H. von Berlepsch, S. Kirstein, R. Hania, A. Pugzlys, and C. Böttcher, *J. Phys. Chem. B*, vol. 111, p. 1701, 2007.

[16] D. M. Eisele, C. W. Cone, E. A. Bloemsma, S. M. Vlaming, C. G. F. van der Kwaak, R. J. Silbey, M. G. Bawendi, J. Knoester, J. P. Rabe, and D. A. Vanden Bout, *Nature Chemistry*, vol. 4, p. 655, 2012.

[17] C. Didraga, A. Pugzlys, P. R. Hania, H. von Berlepsch, K. Duppen, and J. Knoester, *J. Phys. Chem. B*, vol. 108, no. 39, pp. 14976–14985, 2004.

[18] A. Pugzlys, P. R. Hania, R. Augulis, K. Duppen, and P. H. M. van Loosdrecht, *Int. J. of Photoenergy*, vol. 2006, no. 29623, 2006.

[19] J. Sperling, A. Nemeth, J. Hauer, D. Abramavicius, S. Mukamel, H. F. Kauffmann, and F. Milota, *J. Phys. Chem. A*, vol. 114, no. 32, pp. 8179–8189, 2010.

[20] F. C. Spano, *Acc. Chem. Res.*, vol. 43, no. 3, pp. 429–439, 2010.

[21] S. Roy, J. Lessing, G. Meisi, Z. Ganim, A. Tokmakoff, J. Knoester, and T. L. C. Jansen, *J. Chem. Phys.*, vol. 135, no. 15, p. 234507, 2011.

[22] A. G. Redfield, *Advances in Magnetic Resonance,* edited by J. S. Waugh *(Academic Press,* 1965*)*, vol. 1, pp. 1–30.

[23] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy (Oxford University Press,* New York, 1995*)*.

[24] L. Chen, R. Zheng, Q. Shi, and Y. Yan, *J. Chem. Phys.*, vol. 132, p. 024505, 2010.

[25] J. T. Stockburger and H. Grabert, *Phys. Rev. Lett.*, vol. 88, p. 170407, 2002.

[26] H. Torii, *Chemical Physics Letters*, vol. 414, no. 4–6, pp. 417–422, Oct. 2005.

[27] A. Paarmann, T. Hayashi, S. Mukamel, and R. J. D. Miller, *J. Chem. Phys.*, vol. 128, no. 19, p. 191103, May 2008.

[28] T. L. C. Jansen and J. Knoester, *J. Chem. Phys.*, vol. 127, p. 234502, 2007.

[29] T. L. C. Jansen and J. Knoester, *J. Phys. Chem. B*, vol. 110, no. 45, pp. 22910–6, 2006.

[30] C. Liang, M. Louhivuori, S. J. Marrink, T. L. C. Jansen, and J. Knoester, *J. Chem. Phys.*, vol. 138, p. 164106, 2013.

[31] P. Ehrenfest, *Z. Phys.*, vol. 45, p. 455, 1927.

[32] J. C. Tully, *The Journal of Chemical Physics*, vol. 93, no. 2, p. 1061, 1990.

[33] P. V. Parandekar and J. C. Tully, *J. Chem. Phys.*, vol. 122, p. 094102, 2005.

[34] J. R. Schmidt, P. V. Parandekar, and J. C. Tully, *J. Chem. Phys.*, vol. 129, p. 044104, 2008.

[35] R. Tempelaar, C. P. van der Vegte, J. Knoester, and T. L. C. Jansen, *J. Chem. Phys.*, vol. 138, no. 16, p. 164106, Apr. 2013.

[36] P. Hamm and M. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy (Cambridge University Press,* Cambridge, 2011*)*.

[37] J. I. Frenkel, *Phys. Rev.*, vol. 37, p. 17, 1931.

[38] R. Peierls, *Ann. Phys. (Leipzig)*, vol. 13, p. 905, 1932.

[39] J. Knoester, *Optical properties of molecular aggregates,* In V. M. Agranovich and G. C. La Rocca, editors, Proceedings of the International School of Physics "Enrico Fermi" Course CXLIX, pages 149-186. *IOS Press,* Amsterdam, 2002.

[40] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems (*John Wiley & Sons, 2004*)*.

[41] J. C. Tully and R. K. Preston, *J. Chem. Phys.*, vol. 55, p. 562, 1971.

[42] M. Zerner, *Reviews in Computational Chemistry,* Volume 2, edited by K. B. Lipkowitz and D. B. Boyd *(VCH,* New York, 1991*)*, p. 313.

[43] C. Olbrich and U. Kleinekathöfer, *J. Phys. Chem. B*, vol. 114, no. 38, pp. 12427–37, Sep. 2010.

[44] M. E. Madjet, A. Abdurahman, and T. Renger, *J. Phys. Chem. B*, vol. 110, no. 34, pp. 17268–81, Aug. 2006.