Tensor network states simulations of exciton-phonon quantum dynamics for applications in artificial light-harvesting

Florian Alexander Yinkan Nepomuk Schröder
Department of Physics
University of Cambridge

This dissertation is submitted for the degree of
Doctor of Philosophy

Pembroke College September 2017
Tensor network states simulations of exciton-phonon quantum dynamics for applications in artificial light-harvesting

Florian Alexander Yinkan Nepomuk Schröder

Light-harvesting in nature is known to work differently than conventional man-made solar cells. Recent studies found electronic excitations, delocalised over several chromophores, and a soft, vibrating structural environment to be key schemes that might protect and direct energy transfer yielding increased harvest efficiencies even under adversary conditions. Unfortunately, testing realistic models of noise assisted transport at the quantum level is challenging due to the intractable size of the environmental wave function.

I developed a powerful tree tensor network states (TTNS) method that finds an optimally compressed explicit representation of the combined electronic and vibrational quantum state. With TTNS it is possible to simulate exciton-phonon quantum dynamics from small molecules to larger complexes, modelled as an open quantum system with multiple bosonic environments.

After benchmarking the method on the minimal spin-boson model by reproducing ground state properties and dynamics that have been reported using other methods, the vibrational quantum state is harnessed to investigate environmental dynamics and its correlation with the spin system. To enable simulations of realistic non-Born-Oppenheimer molecular quantum dynamics, a clustering algorithm and novel entanglement renormalisation tensors are employed to interface TTNS with \textit{ab initio} density functional theory (DFT). A thereby generated model of a pentacene dimer containing 252 vibrational normal modes was simulated with TTNS reproducing exciton dynamics in agreement with experimental results. Based on the environmental state, the (potential) energy surfaces, underlying the observed singlet fission dynamics, were calculated yielding unprecedented insight into the super-exchange mediated avoided crossing mechanism that produces ultrafast and high yield singlet fission.

This combination of DFT and TTNS is a step towards large scale material exploration that can accurately predict excited states properties and dynamics. Furthermore, application to biomolecular systems, such as photosynthetic complexes, may give valuable insights into novel environmental engineering principles for the design of artificial light-harvesting systems.
To Finlay, Julian, and Molly . . .
Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 60,000 words including abstract, tables, footnotes, and appendices.

Florian Alexander Yinkan Nepomuk Schröder
September 2017
Acknowledgements

I thank Prof. Sir Richard Friend for offering this interdisciplinary PhD with the ambitious aim to simultaneously pursue experimental and theoretical work. Although the theoretical project turned out to be more fruitful in the end, I highly appreciate working in this mostly experimental environment to gain a deeper understanding of and learn to communicate with both worlds in physics.

Many thanks to Dr. Alex Chin for the excellent supervision and guidance he provided over the years. He supported me with the right discussions and ideas at the right time and also allowed me to freely roam in my technical development, which in the end led to the powerful tool I created.

I thank Dr. Akshay Rao, Dr. Frederik Morgenstern, Dr. Andreas Jakowetz, Dr. Felix Deschler and Dr. Nicholas Paul for teaching me how to align lasers and to perform TA measurements.

Many thanks to David Turban, Dr. Nicholas Hine, Dr. Steven Lukman and Dr. Andrew Musser for the fruitful collaboration and many discussions on DP-Mes. I also thank Dr. Anton Potočnik and Prof. Andreas Wallraff, as well as Dr. Johannes Feist and Prof. Francisco Garcia-Vidal for the productive collaborations.

Thanks to all members of the Fastlab, including Maxim, Hannah, Simon, Mike, Ture, Johannes, Jasmine, Vincent, Murad, Matt, Alex, Rene, Brian, Hope, Leah, Jesse, Arya, Limeng, Richard, Qifei, Raj, Peter, et al. for the many social events and discussions that improved my understanding of experimentalists. Thanks to all other members of OE and BSS, especially Sam, Karl, Tobias, Jerome, Robin, Tom, Marcus, Le, Nate, Ned, Greg, Florian, Saul, Arfa, and May Ling for composing this friendly, open, cake-baking and -loving group, for all the cheerful chats over tea, coffee, beer, wine, and whisky.

I thank Dr. Cheng Guo, Prof. Jan von Delft, and Benedikt Bruognolo for introducing me to MPS and for technical discussions. Many thanks to Dr. Carlos Gonzalez-Ballestero, Javier del Pino and Antonis Alvertis for being interested in my work and continuing it.
Many thanks to the OE group, Pembroke College and the Graduate Parlour for offering such a stimulating environment and a place to do this work. I would like to thank the Winton Programme for the Physics of Sustainability, the EPSRC, and Pembroke College for financial support.

I thank Dr. Elisa Hemmig, Dr. Jan Beitner, and Dr. Maxim Tabachnyk for accompanying me on this wonderful journey throughout the masters and PhD.

I particularly thank my mother for the freedom, support and trust in my abilities. Thanks to my family, especially my loving grandmother, for providing me with everything I needed to become the person I am.

I am especially grateful for my partner, Molly, for her ongoing support and hard work to get through the most difficult times in Cambridge and for managing our transition into a new life in Munich. Thank you for our wonderful children, Julian and Finlay. Thanks to my little, young family for plenty of love, nappies, spillage, and more generally, for bringing this very special kind of joy to my life.
# Table of contents

Nomenclature xv

1 Introduction 1

2 Background 5

2.1 Open Quantum Systems ................................. 5
  2.1.1 Description of closed quantum systems ............... 5
  2.1.2 The system and its environment ..................... 6
  2.1.3 Reduced system dynamics - Nakajima-Zwanzig master equation 8
  2.1.4 Markovian master equations .......................... 10
  2.1.5 Advanced master equation methods for open system dynamics . 14
  2.1.6 Observables of the open system ...................... 15
  2.2 The spin-boson model ................................. 16
  2.3 Singlet Fission ...................................... 18
  2.4 Relaxation pathways .................................. 21

3 Computational Methods 23

3.1 Hamiltonian transformation ............................. 24
  3.1.1 Clustering of bosonic modes ......................... 24
  3.1.2 Orthogonal polynomials .............................. 27
  3.2 Matrix Product States and Tree Tensor Networks .......... 33
    3.2.1 Tensor Basics .................................. 35
    3.2.2 Tensor decomposition .............................. 36
    3.2.3 Matrix Product States .................. 39
    3.2.4 Variational ground state optimization .............. 42
    3.2.5 Tree Tensor Network States ................. 43
    3.2.6 Entanglement Renormalisation Tensors ............ 44
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Time-dependent variational principle</td>
<td>48</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Derivation of the tangent space projector</td>
<td>48</td>
</tr>
<tr>
<td>3.3.2</td>
<td>1-tensor update scheme: MPS with OBB</td>
<td>53</td>
</tr>
<tr>
<td>3.3.3</td>
<td>1-tensor update scheme: TTNS</td>
<td>55</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Numeric integration with Krylov subspace technique</td>
<td>58</td>
</tr>
<tr>
<td>3.3.5</td>
<td>Trotter splitting for higher order tensors</td>
<td>59</td>
</tr>
<tr>
<td>3.3.6</td>
<td>Benchmarks and Accuracy of ER-tensors</td>
<td>60</td>
</tr>
<tr>
<td>3.3.7</td>
<td>Benchmarking multi-chain TDVP with the independent boson model</td>
<td>62</td>
</tr>
<tr>
<td>3.4</td>
<td>Dynamic energy surfaces</td>
<td>63</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Introduction: 2-level System</td>
<td>63</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Multi-level Systems</td>
<td>64</td>
</tr>
<tr>
<td>3.5</td>
<td>Transfer Tensors</td>
<td>72</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Ancilla-assisted quantum process tomography</td>
<td>73</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Compression of transfer tensors</td>
<td>74</td>
</tr>
<tr>
<td>3.5.3</td>
<td>Preliminary results for the Ohmic SBM</td>
<td>74</td>
</tr>
<tr>
<td>Appendix 3.A</td>
<td>Lanczos Algorithm</td>
<td>77</td>
</tr>
<tr>
<td>Appendix 3.B</td>
<td>Detection of numerical instability</td>
<td>77</td>
</tr>
<tr>
<td>Appendix 3.C</td>
<td>Imaginary time-evolution for thermal states</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>Spin Boson Model Simulations</td>
<td>81</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>82</td>
</tr>
<tr>
<td>4.2</td>
<td>The spin-boson model</td>
<td>83</td>
</tr>
<tr>
<td>4.3</td>
<td>Ground state properties</td>
<td>83</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Logarithmic discretisation</td>
<td>83</td>
</tr>
<tr>
<td>4.3.2</td>
<td>The Ohmic regime</td>
<td>84</td>
</tr>
<tr>
<td>4.3.3</td>
<td>The independent SBM</td>
<td>85</td>
</tr>
<tr>
<td>4.4</td>
<td>Simulated SBM dynamics</td>
<td>87</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Spin-dynamics</td>
<td>88</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Environment dynamics and spectroscopy</td>
<td>92</td>
</tr>
<tr>
<td>4.5</td>
<td>Conclusions</td>
<td>97</td>
</tr>
<tr>
<td>Appendix 4.A</td>
<td>Convergence of simulations</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>Simulations of Singlet Fission in DP-Mes</td>
<td>101</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>102</td>
</tr>
<tr>
<td>5.2</td>
<td>Electronic structure and vibronic model</td>
<td>103</td>
</tr>
</tbody>
</table>
5.3 Interface to TTNS .................................................. 105
5.4 TTNS for vibronic quantum dynamics ......................... 106
5.5 Simulation Results .................................................. 107
  5.5.1 Fission dynamics in DP-Mes ................................. 107
  5.5.2 Dynamic energy surfaces ................................. 109
5.6 Supporting Results .................................................. 112
  5.6.1 Energy Surfaces ........................................ 113
  5.6.2 Dynamics with fewer modes .......................... 114
  5.6.3 Rabi Dynamics ........................................ 117
  5.6.4 Exclusion of $A_2$ pathway ....................... 118
  5.6.5 LE$^+\rightarrow$T as Landau-Zener transition ............ 119
5.7 Conclusions .................................................. 120
Appendix 5.A Methods .................................................. 121
  5.4.1 DFT ........................................ 121
  5.4.2 Tensor Network States ....................... 126
Appendix 5.B Model parameters ......................................... 127

6 Artificial light-harvesting in superconducting qubits ....... 131
6.1 Introduction .................................................. 133
6.2 Model Hamiltonian and characterisation ......................... 133
  6.2.1 Experimental characterisation .......................... 135
6.3 Deriving observables from the master equation ............... 137
  6.3.1 Lindblad master equation .......................... 137
  6.3.2 Currents ........................................ 138
  6.3.3 Spectral features ....................... 141
6.4 Results .................................................. 142
  6.4.1 Coherent drive and white noise ...................... 142
  6.4.2 Coherent drive and Lorentzian noise .................. 144
  6.4.3 Coherent drive, coherent noise ....................... 147
  6.4.4 Incoherent excitation ....................... 147
6.5 Conclusions .................................................. 150

7 Conclusions and Prospects ........................................ 151
  7.1 Prospects .................................................. 152

List of publications ........................................ 155
References
Nomenclature

Mathematical Symbols

$\hat{n}_k$  Index of OBB of site $k$

$A(k)$  MPS tensor at site $k$

$A_C(k)$  Focused MPS tensor at site $k$

$a_k$  Index of bond $k$

$C_a(k)$  Focused bond centre tensor at bond $k$

$C_{\hat{n}}(k)$  Focused OBB bond centre tensor at site $k$

$D_k$  Bond dimension of bond $k$

$d_k$  Local Hilbert space dimension of site $k$

$d_{OBB,k}$  Dimension of Optimised Boson Basis of site $k$

$H(k)$  Effective Hamiltonian for site $k$

$K(k)$  Effective Hamiltonian for bond center tensor at site $k$

$n_k$  Index of local Hilbert space of site $k$

$V(k)$  OBB tensor at site $k$

$V_C(k)$  Focused OBB tensor at site $k$

$E$  Environment

$\mathcal{H}$  Hilbert Space

$\mathcal{K}$  Memory Kernel
$\mathcal{K}_m$  Krylov subspace of dimension $m$

$\mathcal{L}$  Liouville operator in the interaction picture

$L$  Liouville operator

$L[C]$  Lindblad super-operator

$S$  System

$\mathcal{T}$  Time ordering operator

$\mathcal{W}$  Coupling operator

$\overline{\mathcal{W}}$  Coupling operator, approximated

**Acronyms / Abbreviations**

HEOM  Hierarchical Equations Of Motion

LVC  Linear Vibronic Coupling Model

MPS  Matrix Product States

QPT  Quantum Phase Transition

RDM  Reduced Density Matrix

SBM  Spin Boson Model

TNS  Tensor Network States

TTNS  Tree Tensor Network States

VMPS  Variational Matrix Product States

CT  Charge Transfer state

DFT  Density Functional Theory

DMRG  Density Matrix Renormalisation Group

DP-Mes  13,13’-bis(mesityl)-6,6’-dipentacenyl, Pentacene dimer molecule

ER  Entanglement Renormalisation
Nomenclature

HOMO  Highest Occupied Molecular Orbital
ICS    Intersystem Crossing
irrep  Irreducible Representation
LBO    Local Basis Optimisation
LE     Localised Exciton
LUMO   Lowest Unoccupied Molecular Orbital
MCTDHF Multi-Configurational Time-Dependent Hartree-Fock
ML-MCTDH Multi-Layer Multi-Configurational Time-Dependent Hartree theory
NAT    Noise Assisted Transport
NRG    Numerical Renormalisation Group
OBB    Optimised Boson Basis
OQS    Open Quantum System
PES    Potential Energy Surface
PSD    Power Spectral Density
QED    Quantum Electrodynamics
QHO    Quantum Harmonic Oscillator
QR     QR-Decomposition
RC     Reaction Coordinate
SF     Singlet Fission
SVD    Singular Value Decomposition
t-DMRG Time-Dependent Density Matrix Renormalisation Group
t-SNE  t-Stochastic Neighbour Embedding
TD-DFT Time-Dependent Density Functional Theory
TDVP  Time-Dependent Variational Principle

TEBD  Time-Evolving Block Decimation

TES   Total Energy Surface

TLS   Two-Level System

TT    Triplet pair state

TTM   Transfer Tensor Method
Chapter 1

Introduction

In recent years, people and their leaders started to accept the need for renewable energies to replace fossil fuels as primary energy source, which is reflected in an increasing demand world-wide. While nuclear fusion poses a highly promising technology to serve the base load with, in comparison to nuclear fission, relatively harmless and short-lived radioactive waste, there are a number of areas where solar technologies can be highly valuable. Self-sufficient energy supply for remote areas, mobile devices and transportation are examples where photovoltaics (PV) can reduce the need for heavy, high capacity battery technology or support it to achieve longer lifetimes.

Conventional PV technology involving silicon or III-V semiconductors is already well researched with single-junction (unconcentrated) solar cells reaching efficiencies of 28.8\% [1], very close to the Shockley-Queisser limit of 33.2\%, and state-of-the-art four-junction (concentrated) solar cells reaching 46\% out of a theoretical maximum of 65.1\% [107, 122]. Despite being highly efficient, these solar cells are less accessible to the majority of applications since their production is very expensive and energy intensive. The very recently emerging perovskite materials seem to be a promising low-cost alternative with efficiencies reaching 22.1\% [1], however they still suffer significant stability issues and degrade rapidly under exposure to humidity, oxygen and ultraviolet light [78].

Comparing conventional solar cells with natural light-harvesting pigment-protein complexes (PPC), we can identify substantially different design strategies trying to solve the same challenge of absorbing a photon and using its energy to excite and separate an electron–hole pair. Instead of perfecting a semiconductor single crystal, where any kind of crystal defect causes drops in efficiency, PPCs are highly heterogeneous structures which do not assume a rigid well-defined geometry but exhibit only a certain
regularity and patterns while being in constant motion within their warm and aqueous environment. While the absorption spectrum of our organic solar cells is mainly defined by the choice of molecules and their self-organised aggregation, in PPCs the absorption properties of chlorophylls and carotenoids are tuned by side-group engineering and well defined molecular packing as imposed by the protein environment [81, 124].

Using modified PPCs for light-harvesting is very intriguing since they are made of cheap and abundant elements and could possibly be produced via self-assembly building upon already existing synthesis pathways or by directly using existing organisms. For example, light-harvesting populations of bacteria could be used in self-regenerating low maintenance solar cells, where energy is extracted in the form of ATP and NADPH. Tuning the absorption spectrum of bacterial PPCs to cover the entire solar spectrum with different mutants should be possible in principle, but would require a solid understanding and adopting of the engineering principles employed in PPCs, as well as theoretical models and methods that are able to accurately predict energy transfer processes within and between PPCs.

Natural light-harvesting complexes have been studied for several decades and only recently, there has been growing experimental evidence that quantum effects might play a role in exciton transport. Furthermore, it is believed that the vibrational environment within the PPCs significantly affects exciton transport by dynamically changing chromophore separations and coupling strengths, the degree of exciton delocalisation and more generally, the local energy landscape. Noise assisted transport (NAT) captures these ideas and aims to explain how a noisy vibrational environment, which at first sight would rather diminish quantum effects and lead to energy dissipation, can instead improve energy transport and make it even robust against defects and trap states.

Testing theories requires the simulation of exciton-phonon quantum dynamics which is very demanding due to the large size of the vibrational environment and the associated Hilbert space. The main goal of this work is to advance matrix product states (MPS), a many-body technique that has proven to be very successful in the simulation of open quantum systems in condensed matter theory, in order to efficiently simulate realistic vibronic quantum dynamics from organic molecules to large PPCs.

After giving a brief overview over some theoretical background in Chapter 2, I detail the technical advances that transform MPS into the more general and powerful tree tensor network states (TTNS) method in Chapter 3. In Chapter 4 I test my MPS implementation with a study of the spin boson model (SBM), which is a simple yet
interesting prototype model for exciton-phonon dynamics that is already well studied in literature.

The next step towards simulating real molecules comprises an appropriate interfacing of TTNS with \textit{ab initio} electronic structure methods that can parametrise the exciton-phonon interaction. Since performing these calculations on large PPCs is not yet feasible, we decided to focus on the vibronic dynamics of a pentacene dimer molecule DP-Mes in Chapter 5. This compound exhibits singlet fission, a spin-allowed conversion of a singlet exciton into two triplet excitons at half the singlet energy, which has interesting applications in PV as a carrier multiplication technique that can be used to improve efficiencies of existing silicon solar cells. Due to the symmetry of its molecular structure, DP-Mes is an ideal system to study vibronic quantum dynamics with respect to multiple independent environments across different timescales.

Aside computational method development we also tried to find experimental model systems that could be used to emulate light-harvesting processes and can overcome limitations imposed by approximations and computational resources. Although chemically synthesising molecular arrays would be ideal, we do not yet have enough structural control to freely and precisely influence molecular arrangement. In a collaborative work described in Chapter 6, we use superconducting circuits to perform analog quantum simulations of a minimal light-harvesting model Hamiltonian, to measure NAT under different types of classical environmental noise and different illumination conditions. We demonstrate the high precision and reliability of this method, avoiding issues of sample degradation or ensemble averages, while taking the experiments from weak to strong coupling regimes.

Finally, in Chapter 7 I will summarise the main results and propose future projects.
Chapter 2

Background

In this chapter, I aim to provide a brief summary of background which is relevant for this thesis. Since the majority of the work is about tensor network techniques and their applications to system-environment models, I will give an introduction to open quantum systems and master equations in Section 2.1. Technical details about existing tensor network techniques are presented in Chapter 3, combined with new and original work. In particular, this thesis focuses on exciton-phonon dynamics in a variety of systems, from the spin-boson model to singlet fission and artificial light-harvesting modelled in superconducting qubits, which will be introduced herein.

2.1 Open Quantum Systems

2.1.1 Description of closed quantum systems

A quantum system $S$ characterised by its Hamiltonian $H_S$ is a closed quantum system, if it exists on its own and does not interact with any other object. In this case, the time-evolution of its initial quantum state $|\Psi_S(t_0)\rangle$ is unitary and generated by its Hamiltonian, as obtained by solving the Schrödinger equation

$$i\frac{\partial}{\partial t} |\Psi_S(t)\rangle = H_S(t) |\Psi_S(t)\rangle,$$

(2.1)

$$|\Psi_S(t)\rangle = U_S(t, t_0) |\Psi_S(t_0)\rangle = T e^{-i\int_{t_0}^{t} H_S(t') dt'} |\Psi_S(t_0)\rangle,$$

(2.2)

where we will use the common convention $\hbar = 1$ throughout the dissertation. Here, $T$ induces a chronological time ordering which is necessary to accommodate the time-dependent Hamiltonian. If the Hamiltonian is taken to be time-independent, as is the
case throughout this work, then the unitary time-evolution operator can be simplified to
\[ U_S(t, t_0) |\Psi_S(t_0)\rangle = e^{-iH_S(t-t_0)} |\Psi_S(t_0)\rangle. \] (2.3)

If the system is in a statistical incoherent mixture of individual pure states \(|\Psi_{S,i}\rangle\) with probabilities \(p_i\), then it is in a mixed state which is described by a density matrix
\[ \rho_S(t_0) = \sum_i p_i |\Psi_{S,i}(t_0)\rangle \langle \Psi_{S,i}(t_0)|. \] (2.4)

The time-evolution of a density matrix is described by the Liouville-von Neumann equation
\[ \frac{\partial}{\partial t} \rho_S(t) = -i[H_S, \rho_S(t)] = L_S \rho_S(t), \] (2.5)
\[ \rho_S(t) = \sum_i p_i |\Psi_{S,i}(t)\rangle \langle \Psi_{S,i}(t)| = U_S(t, t_0) \rho_S(t_0) U_S^\dagger(t, t_0), \] (2.6)

with the Liouville super-operator \(L_S\) of \(S\).

### 2.1.2 The system and its environment

As soon as the quantum system \(S\) is in contact (interaction) with an external system \(E\), the above given closed dynamics description of \(S\) starts to fail and we denote \(S\) an open system. Examples for open quantum systems are basically all real quantum systems that we can measure, such as quantum dots or qubits, are open quantum systems. Experimentally, it is impossible to perfectly isolate a quantum system, due to ubiquitous heat (radiation) and due to the need for measurement equipment that needs to be in contact with the system.

In this case, the closed quantum dynamics of the combined systems \(S\) and \(E\) would be generated by their Hamiltonian
\[ H = H_S + H_I + H_E, \] (2.7)
where \(H_I\) is the interaction Hamiltonian between \(S\) and \(E\). While \(E\) can be small in principle, throughout this work, \(E\) is considered to be a large environment (bath), consisting of hundreds of quantum harmonic oscillators. Due to the large combined Hilbert space, the closed dynamics of system and bath cannot be easily calculated with analytic or even conventional numeric methods such as direct diagonalisation.
of $H$. Most of this work, especially Chapter 3, will develop and use MPS/TTNS, a numerical method that is actually able to calculate the closed quantum dynamics by employing elaborate wave function compression techniques, to investigate models where correlations between $S$ and $E$ are essential to the dynamics and cannot be neglected. In order to appreciate the capabilities of MPS, we will present a conventional analytic approach that attempts to find solution to the reduced dynamics of the system $S$, by means of several restrictive approximations, which will be used in Chapter 6.

If $S$ and $E$ are not entangled, then their pure system-environment state is a product state

$$|\Psi\rangle = |\Psi_S\rangle |\phi\rangle,$$  \hspace{1cm} (2.8)

of individual pure system $|\Psi_S\rangle$ and bath states $|\phi\rangle$. Otherwise, as soon as $S$ and $E$ are entangled, $|\Psi\rangle$ can be formally written as

$$|\Psi\rangle = \sum_i s_i |\Psi_{S,i}\rangle |\phi_i\rangle,$$  \hspace{1cm} (2.9)

by using the Schmidt decomposition, with pure and orthogonal bath $|\phi_i\rangle$ and system states $|\Psi_{S,i}\rangle$ and complex probability amplitudes $c_i$. From the corresponding density matrix

$$\rho = |\Psi\rangle \langle \Psi | = \sum_{i,j} s_i s_j^* |\Psi_{S,i}\rangle \langle \phi_i | \langle \phi_j | |\Psi_{S,j}\rangle,$$  \hspace{1cm} (2.10)

it is possible to calculate the reduced density matrix (RDM) of the system $\rho_S$ by performing a partial trace over all bath states

$$\rho_S = \text{tr}_E\{\rho\} = \sum_k \langle \phi_k | \langle \Psi | \langle \Psi | \phi_k \},$$

$$= \sum_i |s_i|^2 |\Psi_{S,i}\rangle \langle \Psi_{S,i} |,$$  \hspace{1cm} (2.11)

$$\hspace{1cm} (2.12)$$

where we used the orthogonality of the bath states. Above expression exhibits that the system’s RDM describes a mixed state as soon as system and environment are entangled. Even if system and environment are initially prepared in a product state, their interaction will eventually lead to entanglement that can be understood in a more general framework as a transfer of information or an increase in entropy as measured by the von Neumann entropy

$$S = -\text{tr}\{\rho \ln \rho\} = - \sum_i p_i \ln p_i,$$  \hspace{1cm} (2.13)
which emphasises the irreversibility of the system-environment mixing. While the emission of energy into the environment is understood as dissipation, the degradation of an initially pure system state into an incoherent mixture is known as decoherence. This exchange of information and energy is the reason for denoting $S$ an open quantum system which has non-unitary dynamics due to the build up of correlations with the bath. If the bath has a finite number of modes there exists a timescale at which recurrences occur and the dynamics are reversible, however for an infinite continuum of bath modes recurrence times become infinite and dynamics become irreversible.

### 2.1.3 Reduced system dynamics - Nakajima-Zwanzig master equation

Typically, the environment is a heat bath $B$ and therefore taken to be in a thermal (mixed) state $\rho_B$ such that the initial system-environment product state is written as

$$\rho(t_0) = \rho_S(t_0) \otimes \rho_B.$$  

(2.14)

As described in full detail in Breuer and Petruccione [17, Ch. 9] and Weiss [137, Ch. 2.3], the equations of motion for the RDM can be obtained by applying a projection operator technique in the interaction picture and solving the resulting coupled differential equations. By changing into the interaction picture with

$$H = H_S + H_E + H_I,$$  

(2.15)

$$U_0(t) = e^{-iH_0(t)},$$  

(2.16)

$$\dot{\rho}(t) = U_0^\dagger(t)\rho(t)U_0(t),$$  

(2.17)

$$\tilde{H}_I(t) = U_0^\dagger(t)H_IU_0(t),$$  

(2.18)

and taking $t_0 = 0$ for simplicity, the dynamics generated by the non-interacting system and environment Hamiltonians are solved by applying them to the operators to simplify the von Neumann equation to

$$\frac{\partial}{\partial t} \dot{\rho}(t) = -[\tilde{H}_I(t), \dot{\rho}(t)] = \mathcal{L}(t)\dot{\rho}(t),$$  

(2.19)
where $\mathcal{L}$ is the interaction picture Liouville operator. The projection operators

$$\mathcal{P} \hat{\rho}(t) = \text{tr}_B \{ \hat{\rho}(t) \} \otimes \hat{\rho}_B,$$

$$\mathcal{Q} \hat{\rho}(t) = (1 - \mathcal{P}) \hat{\rho}(t),$$

are orthogonal to each other and separate the state into $\mathcal{P} \hat{\rho}$, a part that is separable into system RDM and bath $\hat{\rho}_B$, and a part $\mathcal{Q} \hat{\rho}$ that contains all correlations between system and bath, as well as deviations of the environment from $\hat{\rho}_B$. Inserting identities of these projection operators on both sides of Eq. (2.19) yields the coupled differential equations

$$\frac{\partial}{\partial t} \mathcal{P} \hat{\rho}(t) = \mathcal{P} \mathcal{L} \mathcal{P} \hat{\rho} + \mathcal{P} \mathcal{L} \mathcal{Q} \hat{\rho},$$

$$\frac{\partial}{\partial t} \mathcal{Q} \hat{\rho}(t) = \underbrace{\mathcal{Q} \mathcal{L} \mathcal{P} \hat{\rho}}_{\text{inhomogeneous}} + \underbrace{\mathcal{Q} \mathcal{L} \mathcal{Q} \hat{\rho}}_{\text{homogeneous}}.$$

By formally solving homogeneous and inhomogeneous parts of Eq. (2.23) and substituting in Eq. (2.22) we can arrive at the lengthy Nakajima-Zwanzig master equation which we will not state here. For factorising initial conditions Eq. (2.14) and vanishing odd moments of the interaction Hamiltonian with respect to the bath state

$$\langle \hat{H}_I(t_1) \hat{H}_I(t_2) \ldots \hat{H}_I(t_{2n+1}) \rangle \hat{\rho}_B = 0$$

the Nakajima-Zwanzig master equation reduces to

$$\frac{\partial}{\partial t} \mathcal{P} \hat{\rho}(t) = \int_0^t \mathcal{K}(t, s) \hat{\rho}(s) \, ds,$$

$$\mathcal{K}(t, s) = \mathcal{P} \mathcal{L}(t) \mathcal{G}(t, s) \mathcal{Q} \mathcal{L}(s) \mathcal{P};$$

$$\mathcal{G}(t, s) = T \int_s^t Q \mathcal{L} \mathcal{Q} \mathcal{L} \mathcal{Q} \, dr,$$

where $\mathcal{K}$ is known as the memory kernel that captures all effects in $\hat{\rho}_S$ due to the system-bath interaction and $\mathcal{G}$ is the propagator for the subspace projected by $\mathcal{Q}$.

Here, $\mathcal{K}$ is convoluted with $\hat{\rho}(s)$ of all previous times $s < t$ in order to produce the dynamics at time $t$ which exhibits the non-Markovianity of this equation. This equation is exact, but the calculation of the memory kernel is non-trivial since it involves path integrals using the Feynman-Vernon influence functional [25]. One way of calculating the memory kernel numerically using transfer tensors [25] is presented in Sec. 3.5.
2.1.4 Markovian master equations

The Nakajima-Zwanzig equation is the starting point from which different types of master equations can be derived by performing various approximations and perturbative expansions of $K$. In the following we describe the approximations necessary to arrive at the Bloch-Redfield master equation.

In a first step, the memory kernel is expanded perturbatively to second order in the interaction, which results in the simplification $G \approx 1$ to yield

$$\frac{\partial}{\partial t} \tilde{\rho}(t) = \int_0^t \mathcal{P} \mathcal{L}(t) \mathcal{L}(s) \mathcal{P} \tilde{\rho}(s) \, ds,$$

which already contains the Born-Oppenheimer approximation. This approximation assumes a weak coupling between system and environment such that any entanglement between them can be considered negligible. This simultaneously establishes the notion of a bath since it is not influenced by the system. The assumption of vanishing system-bath entanglement is quite restrictive in the physical effects that can be captured by the derived equations. As an example, it is not valid in the vicinity of conical intersections or for non-adiabatic dynamics at avoided crossings of energy surfaces. Within the Born-Oppenheimer approximation, dynamics which started initially in a product state

$$\rho_0 = \rho_{S,0} \otimes \rho_{B,0},$$

$$\rho(t) \approx \rho_S(t) \otimes \rho_B$$

will stay in a product state which is exactly the effect of $\mathcal{P} \tilde{\rho}(s)$. Thus, we can make use of the explicit expression for $\rho$ and find the master equation for the system’s RDM as

$$\frac{\partial}{\partial t} \rho_S(t) = -i[H_S, \rho_S(t)] + U_0(t) \tilde{\rho}_S(t) U_0^\dagger(t),$$

$$\frac{\partial}{\partial t} \tilde{\rho}_S(t) = -\int_0^t \text{tr}_B \left[ \tilde{H}_I(t), \left[ \tilde{H}_I(s), \tilde{\rho}_S(s) \otimes \tilde{\rho}_B \right] \right] \, ds.$$

This equation still contains a convolution over past system states $\tilde{\rho}_S(s)$ for $s \leq t$ which accounts for any effect the past system states had on the environment. If correlations and excitations of the bath decay much faster than the fastest relevant timescale of the system, then one can perform the Markov approximation which simplifies the master
equation to
\[ \frac{\partial}{\partial t} \tilde{\rho}_S(t) = - \int_0^\infty \text{tr}_B \left[ \tilde{H}_I(t), \left[ \tilde{H}_I(t - s), \tilde{\rho}_S(t) \otimes \tilde{\rho}_B \right] \right] \, ds. \] (2.33)

The Markov approximation presumes that the environment has no memory such that its influence on the system only depends on the current state of the system \( \rho_S(t) \) and not on its history \( \rho_S(s) \). This allows replacing any occurrences of \( \rho_S(s) \) by \( \rho_S(t) \), a substitution \( s \to t - s \) and letting the integration bound \( t \to \infty \) to yield this time-local master equation which is easier to integrate. This approximation is valid in the case of baths with continuous spectral densities and large bandwidths compared to system energies, while it fails for narrow, peaked spectral densities with limited bandwidth. For example, Lorentzian spectral densities are typically highly non-Markovian, especially if the characteristic frequency of the peak is comparable to energies of the system.

**The Bloch-Redfield master equation**

To derive the Bloch-Redfield master equation from the Markovian quantum master equation, an explicit form of the interaction Hamiltonian has to be used

\[ H_I = \sum_\alpha A^\alpha \otimes B^\alpha, \] (2.34)

with interaction operators \( A^\alpha \) of the system and \( B^\alpha \) of the bath. In a first step, the system Hamiltonian is diagonalised and the operators \( A^\alpha \) are decomposed into

\[ A^\alpha = \sum_\omega A^\alpha(\omega), \] (2.35)

where each \( A^\alpha(\omega = \epsilon_n - \epsilon_m) \) mediates an elementary transition from the eigenstate of energy \( \epsilon_n \) to the level with energy \( \epsilon_m \). Thus the interaction picture Hamiltonian becomes

\[ \tilde{H}_I(t) = U_0^\dagger(t) \left( \sum_{\alpha, \omega} A^\alpha(\omega) \otimes B^\alpha \right) U_0(t) \] (2.36)

\[ = \sum_{\alpha, \omega} e^{-i\omega t} A^\alpha(\omega) \otimes \tilde{B}^\alpha(t), \] (2.37)
which can be substituted in Eq. (2.33) to give eventually

\[
\frac{\partial}{\partial t} \tilde{\rho}_S(t) = \sum_{\omega, \omega'} \sum_{\alpha, \beta} e^{i(\omega' - \omega)t} \Gamma^{\alpha\beta}(\omega) \left( A^\beta(\omega)\tilde{\rho}_S(t)A^\alpha(\omega') - A^\alpha(\omega')A^\beta(\omega)\tilde{\rho}_S(t) \right) + h.c,
\]

(2.38)

\[
\Gamma^{\alpha\beta}(\omega) = \int_0^\infty ds \ e^{i\omega s} \langle \tilde{B}^\alpha(s)\tilde{B}^\beta(0) \rangle_{\rho_B},
\]

(2.39)

where the trace over the bath states and operators is collected in the Fourier transform \( \Gamma^{\alpha\beta} \) of the bath correlation functions. For stationary bath states \( \rho_B \) the correlation functions are homogeneous and can be calculated as

\[
\Gamma^{\alpha\beta}(\omega) = \int_0^\infty ds \ e^{i\omega s} \langle \tilde{B}^\alpha(s)\tilde{B}^\beta(0) \rangle_{\rho_B} \delta_{\alpha,\beta}.
\]

(2.40)

While usually the correlations between bath operators with \( \alpha \neq \beta \) are kept for the sake of generality, in this work we will consider non-interacting environments, where each bath mode is exclusively coupled to the system, such that there are no correlations between different bath oscillators

\[
\Gamma^{\alpha\beta}(\omega) = \int_0^\infty ds \ e^{i\omega s} \langle \tilde{B}^\alpha(s)\tilde{B}^\beta(0) \rangle_{\rho_B} \delta_{\alpha,\beta}.
\]

(2.41)

Therefore, we can simplify above equations to

\[
\frac{\partial}{\partial t} \tilde{\rho}_S(t) = \sum_{\omega, \omega'} \sum_{\alpha} e^{i(\omega' - \omega)t} \Gamma^{\alpha}(\omega) \left( A^\alpha(\omega)\tilde{\rho}_S(t)A^\alpha(\omega') - A^\alpha(\omega')A^\alpha(\omega)\tilde{\rho}_S(t) \right) + h.c,
\]

(2.42)

\[
\Gamma^{\alpha}(\omega) = \int_0^\infty ds \ e^{i\omega s} \langle \tilde{B}^\alpha(s)\tilde{B}^\alpha(0) \rangle_{\rho_B} = \frac{1}{2} S^\alpha(\omega) + i\lambda^\alpha(\omega),
\]

(2.43)

where \( S^\alpha(\omega) = \int_{-\infty}^\infty ds \ e^{i\omega s} \langle \tilde{B}^\alpha(s)\tilde{B}^\alpha(0) \rangle_{\rho_B} \) is the real and positive noise power spectral density inducing transitions, and \( \lambda^\alpha(\omega) \) leads to a renormalisation of system eigenenergies, similar to the Lamb shift, through the Hamiltonian (for \( \omega = \omega' \))

\[
H_{LS} = \tilde{H}_{LS} = \sum_\omega \sum_\alpha \lambda^\alpha(\omega)A^\alpha(\omega)A^\dagger A^\alpha(\omega).
\]

(2.44)
In the Schrödinger picture we get

\[
\frac{\partial}{\partial t} \rho_S(t) = -i[H_S + H_{LS}]\rho_S(t) + R\rho_S(t) , \tag{2.45}
\]

\[
R\rho_S(t) = \frac{1}{2} \sum_{\omega,\omega'} \sum_{\alpha} S^\alpha(\omega) \left( A^\alpha(\omega)\rho_S(t)A^\alpha(\omega')^\dagger - A^\alpha(\omega')^\dagger A^\alpha(\omega)\rho_S(t) \right) + h.c, \tag{2.46}
\]

where the Redfield super-operator \( R \) was used. For numerical applications this equation can be formulated in tensor format

\[
\dot{\rho}_{ab} = -i(\omega_a - \omega_b)\rho_{ab} + R_{abcd}\rho_{cd}, \tag{2.47}
\]

with the Redfield tensor \( R_{abcd} \), where we omitted the renormalisation \( H_{LS} \) which is valid for already assumed weak coupling. Since this equation is simplest in the eigenbasis of \( H_S \), we accordingly transform the operators \( A^\alpha \)

\[
A^\alpha(\omega = \epsilon_n - \epsilon_m) = A^\alpha_{mn}, \tag{2.48}
\]

\[
A^\alpha(\omega = \epsilon_n - \epsilon_m)^\dagger = A^\alpha(-\omega) = A^\alpha_{nm} \tag{2.49}
\]

where the specific transition operator \( A^\alpha(\omega) \) is represented by a single matrix element \( A^\alpha_{mn} \) of the full system operator. In this basis, the noise power spectrum can be put into matrix form \( S^\alpha(\epsilon_n - \epsilon_m) = S^\alpha_{nn} \), and the Redfield tensor becomes

\[
R_{abcd} = \frac{1}{2} \sum_{\alpha} \left[ A^\alpha_{ac} A^\alpha_{bd}(S^\alpha_{ac} + S^\alpha_{db}) - \delta_{bd} \sum_{n} A^\alpha_{na} A^\alpha_{nc} S^\alpha_{nc} - \delta_{ac} \sum_{n} A^\alpha_{nd} A^\alpha_{nb} S^\alpha_{bn} \right] , \tag{2.50}
\]

containing information about all possible transitions caused by \( A^\alpha \), weighted by the noise power spectrum of the bath. The diagrammatic representation of the contraction \( R_{abcd}\rho_{cd} \) in Fig. 2.1 gives a more intuitive picture of the 2nd order processes that are captured in the Redfield tensor.

This master equation does not necessarily conserve positivity of the RDM, meaning that it can lead to negative populations in the time-evolution. This problem does not exist if the coupling is weak enough.

**The Lindblad master equation**

The Lindblad master equation can be derived from the Bloch-Redfield master equation by employing the secular approximation, which neglects any terms which represent non-resonant processes. Thus, terms containing \( e^{i(\omega' - \omega)t} \) for \( \omega' \neq \omega \) in Eq. (2.42) are
considered negligible if they are fast oscillating compared with the typical relaxation time of the system.

This approximation reduces the Redfield super-operator to

$$R \rho_S(t) = \frac{1}{2} \sum_{\omega} \sum_{\alpha} S^\alpha(\omega) [A^\alpha(\omega), \rho_S(t) A^\alpha(\omega)] + h.c., \quad (2.51)$$

which is commonly written more compact in the Lindblad master equation by combining indices \((\omega, \alpha) \rightarrow i\) and replacing symbols \(A \rightarrow C, S \rightarrow \Gamma\) as

$$\dot{\rho}_S = -\frac{i}{\hbar} [\hat{H}, \rho_S] + \sum_i \frac{\Gamma_i}{2} L[C_i] \rho_S, \quad (2.52)$$

$$L[C] \rho_S = 2C \rho_S C^\dagger - \{C^\dagger C, \rho_S\} = [C, \rho_S C^\dagger] + h.c., \quad (2.53)$$

with the Lindblad super-operator \(L[C_i]\), collapse operators \(C_i\) and the rates \(\Gamma_i\) as given by the noise power spectra. The \(C_i\) describe incoherent decay, excitation, and dephasing. Since the Lindblad master equation is trace-preserving and completely positive it does not suffer the negativity issues of the Bloch-Redfield equation.

### 2.1.5 Advanced master equation methods for open system dynamics

There are plenty of other methods which can be employed to treat open quantum systems that try to avoid the restrictions imposed by the approximations mentioned
above. We will not go into much detail but merely mention them to give an overview and to guide the reader.

The polaron transformation is a unitary transformation that can transform the spin-boson Hamiltonian into a more optimal basis such that even intermediate to strong coupling regimes can be studied (see [89, 90]).

The reaction coordinate mapping transforms the Hamiltonian, such that a representative reaction coordinate is generated and included into the system, while a residual bath spectral density is treated perturbatively in its interaction with the system [58]. This approach is well suited for strong coupling and partly non-Born-Oppenheimer dynamics since it allows non-perturbative treatment of the immediate interactions. As a result of the transformation, the coupling to the residual environment can decrease depending on the original spectral density. In this case the weak interaction with the residual environment can be treated with a master equation as described above.

The hierarchical equations of motions (HEOM) is a powerful method to simulate exact quantum dynamics for $\rho_S(t)$ [61, 119]. Due to its complexity it is limited in the types of spectral densities it can simulate. The method has been applied successfully to predict spectra of 2D electronic spectroscopy of light-harvesting complexes [59, 115].

### 2.1.6 Observables of the open system

After finding ways to calculate the time-dependent RDM of the system, we can calculate the expectation value of an observable $A$ as

$$\langle A(t) \rangle = tr \{ A \rho_S(t) \} .$$

In addition, we can calculate derivatives of observables directly from the Lindblad master equation

$$\frac{d}{dt} \langle A(t) \rangle = tr \{ A \dot{\rho}_S(t) \} = i \langle [H, A] \rangle + \sum_i \frac{\Gamma_i}{2} \langle [C_i^\dagger, A] C_i + C_i^\dagger [A, C_i] \rangle_{\rho_S} ,$$

where we exploited the cyclic property of the trace and assumed a time-independent Observable $A$. The terms generated by $i[H, A]$ correspond to coherent contributions, while the terms $[C_i^\dagger, A] C_i + h.c.$ represent incoherent processes. This expression can be very useful in the calculation of currents within a network, such as employed in Chapter 6.
2.2 The spin-boson model

One of the most widely studied and generic system-environment models is the spin-boson model (SBM) [69, 71, 137]. It describes the interaction between a 2-level system, the spin, and a collection or continuum of bosonic modes. Despite its seeming simplicity, it has only a few analytic regimes and is very challenging to treat numerically due to its large Hilbert space. The SBM can be used to model a vast variety of physical problems, since the bosons can represent environments involving, for example, molecular vibrational modes, phonons, and photons. This makes it interesting and highly relevant for materials discovery and photo-physical studies.

The typical SBM Hamiltonian is defined by its system $H_S$ and its bosonic environment with the power-law spectral density $J(\omega)$

$$ H = \frac{\Delta}{2} \sigma_x + \frac{\varepsilon}{2} \sigma_z + \sum_n \omega_n b_n^\dagger b_n + \frac{\sigma_z}{2} \sum_n \lambda_n (b_n + b_n^\dagger), $$

(2.56)

$$ J(\omega) = \pi \sum_n \lambda_n^2 \delta(\omega - \omega_n) = 2\pi \alpha \omega_c^{1-s} \omega^s e^{-\frac{\omega}{\omega_c}}, $$

(2.57)

where $\Delta$ is the tunnelling amplitude between the two spin-states separated by the level bias $\varepsilon$. The bosonic environment consisting of quantum harmonic oscillators of energy $\omega_n$ is coupled diagonally to the two-level system with the coupling constants $\lambda_n$. In the continuum limit, the spectral density can have a soft exponential energy cut-off on the characteristic energy scale $\omega_c$. As $J(\omega)$ peaks at $\omega = s\omega_c$ and $\Delta, \varepsilon \ll \omega_c$, the spectrum is usually taken to be

$$ J(\omega) = 2\pi \alpha \omega_c^{1-s} \omega^s \theta(\omega_c - \omega), $$

(2.58)

to simplify analytical expressions. The high energy cut-off $\omega_c$ of the bath defines the maximum energy scale of the model and is usually taken to be much larger than the other quantities, but is not restricted to it. This hard cut-off is beneficial for MPS calculations using the orthogonal polynomial chain mapping, since a finite bandwidth leads to an upper bound for chain site energies and couplings which limits the speed at which information is transferred down the chain and therefore sets the required minimal chain length.

The SBM is split into the three regimes with sub-Ohmic ($s < 1$), Ohmic ($s = 1$) and super-Ohmic ($s > 1$) damping through the bath. The ground state of the SBM
is one of the most studied topics in condensed matter. The Ohmic and sub-Ohmic SBM have a range of quantum phase transitions (QPT) between a delocalised and localised phase at a critical coupling $\alpha_c$, which have been studied extensively with different numerical techniques, such as the numerical renormalisation group (NRG) [20, 69, 70, 128], quantum Monte Carlo [140], exact diagonalisation [7], density matrix renormalisation group (DMRG) and matrix product states (MPS) [43, 50, 53], and the polaron Ansatz [27, 110]. It has been shown that the ohmic SBM can be mapped to the anisotropic Kondo problem and the resonant level model for which $P(E)$ theory and the Bethe Ansatz exist [69, 137]. I will use the Ohmic regime to test the variational MPS ground state optimisation (VMPS) in Sec. 4.3.2 and compare it qualitatively against the Bethe Ansatz.

Further dynamical studies in Sec. 4.4 will be performed on all regimes, to test the time-evolution using the time-dependent variational principle (TDVP), which has been studied previously by means of time-dependent NRG (TD-NRG) [92], which also shows the failure of Bloch-Redfield master equation approaches, quasiadiabatic propagator path integral (QUAPI) [88], multi-layer multi-configurational time-dependent Hartree theory [133–135], Dirac-Frankel principle with Davydov Ansatz [144], real-time path integral Monte Carlo (PIMC) [63], time evolving density matrix using orthogonal polynomials algorithm (TEDOPA) combined with transfer tensor method (TTM) [102], and HEOM [34].

The independent boson model is a special case of the SBM with $\Delta = 0$ and can be solved analytically since the spin operator commutes with the interaction Hamiltonian [17, Ch. 4.2]. After preparing an initial coherence between upper and lower state with $\langle \sigma_x \rangle = 1$, the time-evolution of the coherence is given analytically by

$$\rho_{12}(t) = \rho_{12}(0)e^{-\Gamma(t)},$$  \hspace{1cm} (2.59)

$$\Gamma(t) = \int_0^\infty J(\omega) \frac{1 - \cos \omega t}{\omega^2} \coth \frac{\beta \omega}{2} \, d\omega. $$  \hspace{1cm} (2.60)

Since we perform calculations at $T = 0$ we can simplify $\coth \frac{\beta \omega}{2} \rightarrow 1$.

By increasing the dimensionality of the system to accommodate all electronic states and therefore allowing multiple, different coupling operators, the SBM can be generalised to a linear vibronic coupling model

$$\hat{H}_{LVC} = H_S + \sum_{n=1}^N W_n \left( \hat{b}_n^\dagger + \hat{b}_n \right) \sqrt{2} + \omega_n \hat{b}_n^\dagger \hat{b}_n, $$  \hspace{1cm} (2.61)
that can be used to model exciton-phonon dynamics in organic molecules (see Sec. 3.1). For more clarity, we will use bold notation for system operators and hats to indicate environmental operators, where necessary. As a result of the larger system dimension, there are more distinct coupling operators that can be used which leads inherently to a multi-environment model. This approach will be used in Chapter 5 to study singlet fission dynamics in a dimer molecule.

### 2.3 Singlet Fission

In organic molecules, optically excitable singlet exciton states $S_1$ can undergo conversion into a pair of spin entangled triplet exciton states (TT) of overall singlet character by sharing energy with a neighbouring ground state molecule. This spin allowed process called singlet fission (SF) can happen on a timescale from 80 fs, as in polycrystalline pentacene, up to 10 ns in pentacene dimers with a bicyclooctane spacer, and can reach triplet yields of up to 200% [65, 98, 112, 113, 138, 148]. Since SF creates two triplet excitons at half the singlet energy from a single photon, SF can help realising organic solar cells with two bandgaps which can help to overcome the Shockley-Queisser limit of single-junction solar cells [107]. This type of carrier multiplication has advantages over conventional tandem solar cells, as it avoids the need for matching the electric current or voltage if solar cells are wired in series or parallel, respectively.

Furthermore, after the decorrelation of the TT state the individual triplet states are better protected against recombination into the ground state than singlet states, since the emission of a photon via phosphorescence and reverse intersystem crossing are spin-forbidden and can only happen through random spin-flips. This leaves more time for charge separation or energy extraction into other materials such as nanocrystals [117].

SF has been observed in a variety of molecules, such as carotenoids [87], conjugated polymers [68], and polyacenes such as tetracene [23, 79, 84, 114] and especially pentacene, which has been studied extensively [35, 97, 98, 117, 129, 139, 145]. Since SF happens on neighbouring molecules, the rate and yield depend not only on the energy level alignment between singlet and triplet, but also on many morphological factors such as the phase (single crystal, polycrystalline, solution), crystal packing, intermolecular spacing via side chains, and the mutual orientation of molecules. The control over these factors pose a significant challenge. As an example, SF can happen very quickly in polycrystalline thin films as molecules are close together, whereas SF
in solution is at least an order of magnitude slower and concentration dependent due to diffusion limitation [129, 139].

A more thorough study of SF and its dependence on mutual orientation of molecules is difficult since control over crystal packing is very limited and measurements are always influenced by ensemble averages. In an attempt to achieve a better control over the molecular orientation, a variety of dimers were studied recently focusing on intramolecular SF [32, 51, 62, 65, 76, 77, 121]. These systems have the advantage of limiting the degree of freedom between the two molecules such that SF can be observed in a very well defined geometry and high order. Furthermore, the reduction of the number of involved molecules by studying dimers in highly diluted solutions, allows better comparisons between experimental results and theoretical investigations by means of electronic structure calculations.

Of particular interest are the underlying mechanisms of SF and to what extent they affect reaction rates and yields. Possible mechanisms include a direct pathway from S_1 to TT [23, 45, 152] and an indirect charge transfer (CT) mediated mechanism [11, 14–16, 83, 120, 149] (see Fig. 2.2). Since it is very difficult to measure CT states
Fig. 2.3 The states relevant for SF in DP-Mes and their symmetries in the point group $D_{2d}$. The lines indicate the vibrational coupling and the symmetry of the corresponding vibrational modes. The grey couplings involve 2 electron interactions and are negligibly small.

and their participation in SF experimentally and since the CT states can be several 100 meV above the singlet state, there are arguments against the CT pathway being involved in ultrafast singlet fission. Additionally, it is not yet clear how SF is affected by or dependent on intra- and inter-molecular vibrations (phonons), as they offer the possibility of dynamically switching and especially increasing certain couplings and pathways [32, 37, 65, 80, 86, 147].

To address these issues, we will specialise in Chapter 5 on a pentacene dimer (DP-Mes) which exhibited fast singlet fission despite having an orthogonal ground state geometry which completely decouples the electronic system [76, 77] and turns off the direct mechanism. The only couplings in this molecule arise from vibrational motion breaking the $D_{2d}$ symmetry of the ground state which can open pathways to the CT manifold as indicated in Fig. 2.3. Density functional theory confirmed that even with symmetry breaking the direct coupling between the localised singlet exciton states $\text{LE}^\pm$ and the TT is negligibly small since it involves a two-electron exchange integral. In addition, symmetry analysis of the vibrational modes and electronic states yields that only certain subsets of modes can couple certain transitions, which requires a multi-environment treatment. Thus, DP-Mes is an ideal candidate to study SF in a
2.4 Relaxation pathways

There are several decay mechanisms for singlet and triplet excitons which have to be considered, as shown in Fig. 2.4. A highly excited singlet exciton $S_n$ can relax rapidly down to $S_1$ via non-radiative pathways, converting the energy mostly into heat. This internal conversion happens within the first hundreds of femtoseconds and is also the dominant relaxation process of higher lying triplet states $T_n$. The singlet state can also undergo inter-system crossing into a triplet state by flipping one spin via strong spin-orbit coupling. This is enhanced close to heavy atoms and strongly suppressed in their absence. The radiative decay of singlet states, called fluorescence, can have lifetimes of $\tau \sim 10^{-8}$ s. Triplet states instead decay very slowly since both, radiative and non-radiative transition to $S_0$, require a spin-flip with lifetimes of $\tau \sim 0.01 - 10$ s.

Fig. 2.4 Summary of optical transitions (blue, red) and non-radiative relaxation channels in a single molecule. Figure from Dr. S. Albert-Seifried with permission [3].
Chapter 3

Computational Methods

In this chapter, I give an introduction to matrix product states (MPS), summarising existing techniques (see Sec. 3.2), as well as describing the tensor network methods that I developed to generate the results presented in Chapters 4 and 5. First, I describe in Section 3.1 a method that transforms a linear vibronic model Hamiltonian, that can be generated in preceding electronic structure calculations, by means of a clustering technique into a multi-environment Hamiltonian suitable for simulations with tensor networks. Thereafter, I explain how a basic MPS can be upgraded step-by-step to a tree tensor network state (TTNS) for multi-environment Hamiltonians in Section 3.2.5. After having defined the structure of a TTNS, I focus on my adaptation of the time-dependent variational principle (TDVP) to non-standard MPS networks with auxiliary tensors, which leads towards the development of a time-evolution scheme for arbitrary TTNS in Section 3.3. I will also describe a new approach to calculate energy surfaces for non-Born-Oppenheimer dynamics, which can reveal the mechanism of entangled system-bath dynamics in Section 3.4.

To the best of my knowledge, this is the first time that tree tensor networks have been constructed based on the analysis of the entanglement properties of a higher order tensor, and that the resulting TTNS has been used to simulate vibronic dynamics of realistic molecules, treated in an open quantum system framework. The simulation code that was developed here is publicly available at GitHub.\footnote{https://github.com/FlorianSchroeder/TTNS-TDVP}

Sections 3.1.2, 3.2.3, 3.3.1, and 3.3.2 have been published in [104], F. A. Y. N. Schröder and A. W. Chin, Physical Review B 93, 075105 (2016). © 2016 by the American Physical Society. Sections 3.1.1, 3.3.3, and 3.4 are contained in the submission, F. A. Y. N. Schröder, D. H. P. Turban, A. J. Musser, N. D. M. Hine, and A. W. Chin,
Multi-dimensional Tensor Network Simulation of Open Quantum Dynamics in Singlet Fission.

3.1 Hamiltonian transformation

For the efficient application of MPS to Hamiltonian models it is important to transform the Hamiltonians such that the number of nearest neighbours is minimised for each quantum object. For a collection of bosonic modes which couple to the system via the same coupling operator this can be achieved with the orthogonal polynomials transformation described in Sec. 3.1.2. However, when interfacing MPS with ab initio electronic structure calculations to simulate the exciton-phonon dynamics of single molecules or larger molecular complexes, the exciton-phonon coupling patterns can be very diverse, depending on the symmetries of the molecule(s). To still allow efficient chain transformations we therefore make use of a clustering algorithm as explained in the following section to identify groups of modes that can be chain transformed to yield a multi-chain star Hamiltonian $\hat{H}_{\text{star}}$. For illustration purposes we apply the clustering to the model Hamiltonian of DP-Mes (Ch. 5).

3.1.1 Clustering of bosonic modes

Model Hamiltonians for exciton-phonon interactions that can be constructed using DFT/TD-DFT simulations, typically assume the linear vibronic coupling form

$$\hat{H}_{\text{LVC}} = \hat{H}_S + \sum_{n=1}^{N} W_n \left( \hat{b}_n^\dagger + \hat{b}_n \right) + \omega_n \hat{b}_n^\dagger \hat{b}_n, \quad (3.1)$$

where $W_n$ are the individual coupling operators in the system Hilbert space for each mode $b_n$ (see Fig. 3.3).

The aim is to find a minimal number of distinct and fixed coupling patterns $\overline{W}_i$, each forming an independent environment $i$, such that all $W_n$ can be assigned to clusters $i$ while optimally fulfilling

$$W_n^{(i)} = \overline{W}_i \lambda_{i,n}, \quad (3.2)$$

if $n$ was assigned to $i$, where $\lambda_{i,n}$ is a scaling factor, equivalent to the coupling strength. We achieve this partition by using the unsupervised machine learning method $k$-means clustering [9], where the cluster centroids represent the approximate (mean) optimal
Fig. 3.1 2D-Projection of the normalised vectorised coupling matrices $W_n$ of DP-Mes using t-SNE already reveals environments of different symmetry. The crosses represent the cluster centroids $\overline{W}_i$ and colours the assigned modes. Especially the ring structure makes it necessary to split $B_2$ into at least two baths.
system coupling operator $W_i$. This variational algorithm starts from a predefined number of clusters $k$ to look for and iteratively optimises initial randomly placed centroids (cluster centres). The optimisation is achieved, by assigning modes to clusters and calculating more optimal centroids based on the assignment until convergence is reached.

To obtain accurate results, we restrict the parameters to the non-zero upper right triangular part of $W_n$, since the coupling operator is always real and symmetric or at least hermitian. This reduces the search space and conserves the symmetry. Furthermore, we normalise the vector containing these parameters to impose the condition that the centroid has to lie on the unit sphere, keeping the overall coupling constant. If the $W_n$ of a single cluster are not ideally linearly dependent but spread with a little variation, then replacing the operator by $W_i$ only yields an approximation

$$W_n^{(i)} = W_i \lambda_{i,n} + \epsilon_n,$$

with the approximation error $\epsilon_n$ for each mode. To minimise the total approximation error

$$\epsilon = \sqrt{\sum_n \|\epsilon_n\|^2_F},$$

where the Frobenius norm is most suitable, we find the cluster centroid $W_i$ as the centre of mass with $\lambda_{i,n}$ taking the role of the mass (weight), such that strongly coupled modes are approximated more accurately since they are more likely to dominate the dynamics.

The approximation error $\epsilon$ depends strongly on the number of clusters $k$. For larger $k$ the error reduces, but in turn the computational effort of TTNS increases, thus we need to find an optimal number of $k$ clusters that compromises between TTNS efficiency and minimal approximation. An objective t-SNE projection [125] of the couplings (Fig. 3.1) can give an idea of whether there are clusters, and it can reveal an approximate number. In this example we can identify a minimum of four clusters, which also agree with the irreps $A_1, A_2, B_1$, and $B_2$ as obtained from group theory. However, since the clusters are fairly broad, our cluster analysis yields that at least seven clusters (coloured as in Fig. 5.3) are necessary for an accurate representation, thus subdividing irreps $A_1, B_1$, and $B_2$. In Figure 3.2 the mean absolute error and standard deviation between the original coupling matrices and the centroid approximations are given for $k \leq 30$. By replacing $W_n^{(i)}$ with the approximation $W_i \lambda_{i,n}$ based on the
cluster centroids, we arrive at the clustered linear vibronic coupling Hamiltonian

\[ \hat{H}_{LVC} = \hat{H}_S + \sum_{i=1}^{7} \sum_{n=1}^{N_i} \left( \lambda_{i,n} \left( \hat{b}_{i,n}^\dagger \hat{b}_{i,n} + \frac{\hat{b}_{i,n}^\dagger \hat{b}_{i,n}}{\sqrt{2}} \right) + \omega_{i,n} \hat{b}_{i,n}^\dagger \hat{b}_{i,n} \right), \]  

(3.5)

where \( N_i \) is the number of modes in cluster \( i \). In the following section we describe how each cluster can be transformed onto a 1D-chain.

### 3.1.2 Orthogonal polynomials

The mapping of the environment to a semi-infinite chain model is performed using orthogonal polynomials as described in Ref. [26, 142], which we summarise in a brief description. The star Hamiltonian

\[
\hat{H} = \hat{H}_S + \int_0^{x_{\text{max}}} g(x) \hat{b}_x^\dagger \hat{b}_x \, dx + \hat{A} \int_0^{x_{\text{max}}} h(x) \left( \hat{b}_x + \hat{b}_x^\dagger \right) \, dx,
\]  

(3.6)
Fig. 3.3 In the first step, the initial linear vibronic coupling model is analysed and approximated via $k$-means clustering to identify independent environments. Secondly, orthogonal polynomials are used to transform each environment onto equivalent 1D-chain models to minimize the number of nearest neighbours for system (S) and the modes. In the resulting star Hamiltonian $\hat{H}_{\text{star}}$ we denote the modes closest to the system as reaction coordinates (RC).
with the system Hamiltonian $H_S$ and the system operator $\hat{A}$ in the interaction term, is mapped onto the chain Hamiltonian

$$H = H_S + \hat{A}c_0 \left( a_0 + a_0^\dagger \right) + \sum_{k=0}^\infty \left[ \omega_k a_k^\dagger a_k + t_k \left( a_k^\dagger a_{k+1} + a_{k+1}^\dagger a_k \right) \right]. \quad (3.7)$$

For an arbitrary spectral density $J(\omega)$ the mapping can be obtained by finding the recurrence relation of polynomials orthogonal with respect to the weight function

$$h^2(x) = J(g(x)) \frac{g'(x)}{\pi}, \quad (3.8)$$

where usually the linear dispersion relation $g(x) = \omega_c x = \omega$ is used without loss of generality. If such a set of polynomials cannot be found analytically, a numerical procedure can be performed as described towards the end of this section.

The orthonormal polynomials $\tilde{p}_k(x)$ generating the orthogonal transformation $U_k(x)$ from the continuous variable $x$ onto the discrete chain

$$U_k(x) = h(x)\tilde{p}_k(x),$$

$$a_k^\dagger = \int_0^{x_{max}} U_k(x) b_k^\dagger \, dx, \quad (3.9)$$

satisfy the normalization condition

$$\langle \tilde{p}_k, \tilde{p}_l \rangle_\mu = \int_0^{x_{max}} h^2(x) \tilde{p}_k(x) \tilde{p}_l(x) \, dx = \delta_{k,l}, \quad (3.10)$$

and relate the monic orthogonal polynomials $\pi_k(x)$ via

$$\tilde{p}_k(x) = \frac{\pi_k(x)}{\|\pi_k(x)\|_\mu}, \quad (3.11)$$

where the norm $\|p\|_\mu = \sqrt{\langle p, p \rangle_\mu}$ is induced by the inner product $\langle \cdot, \cdot \rangle_\mu$ under the measure $d\mu(x) = h^2(x)dx$. The chain parameters $c_0, \omega_k, t_k$ are related to the coefficients
\( \alpha_k, \beta_k \) of the monic recurrence relation

\[
\pi_{k+1}(x) = (x - \alpha_k) \pi_k(x) - \beta_k \pi_{k-1}(x),
\]

\[
\omega_k = \omega_c \alpha_k,
\]

\[
t_k = \omega_c \sqrt{\beta_{k+1}},
\]

\[
c_0 = \|\pi_0(x)\|_\mu,
\]

with the initial polynomials \( \pi_{-1}(x) = 0 \) and \( \pi_0(x) = 1 \).

For the power-law spectral density with hard cut-off at the characteristic frequency \( \omega_c \),

\[
J(\omega) = 2\pi \alpha \omega^{1-s} \theta(\omega_c - \omega),
\]

the site energies \( \omega_k \) and couplings \( c_0, t_k \) can be analytically found as

\[
\omega_k = \frac{\omega_c}{2} \left( 1 + \frac{s^2}{(s + 2k)(2 + s + 2k)} \right),
\]

\[
t_k = \frac{\omega_c (1 + k) (1 + s + k)}{(s + 2 + 2k)(3 + s + 2k)} \sqrt{\frac{3 + s + 2k}{1 + s + 2k}},
\]

for \( k = 0, 1, \ldots, L - 2 \) if the chain is truncated to length \( L \).

**Numeric mapping**

For arbitrary, smooth \( J(\omega) \), or discrete spectral densities, such as the \textit{ab initio} vibrational environment of DP-Mes, which do not have an analytical solution with a pleasant set of recurrence coefficients the orthogonal polynomials mapping can be used in form of the discrete Stieltjes algorithm [48]. The Stieltjes algorithm is qualitatively equivalent to the Lanczos algorithm but considerably faster and numerically less stable [67] (see Fig. 3.4). While any type of discretisation of smooth \( J(\omega) \) can be performed in principle, linear and logarithmic discretisations are the most common choices. In particular, the logarithmic discretisation performs well for calculating low energy ground state properties, while for time-evolution it needs an averaging scheme over multiple calculations to minimize discretisation errors. A very fine linear discretisation instead can yield accurate results in a single simulation. As a result of the discretisation, the map \( U_k(x) \) turns into the matrix \( U_{xk} \).

Due to its speed, the Stieltjes algorithm allows a very fine linear discretisation that asymptotically reaches the analytic mapping results (see Fig. 3.5). Therefore
3.1 Hamiltonian transformation

Fig. 3.4 The Stieltjes method can be unstable, as exposed by this transformation of an ohmic spectral density with $\alpha = 0.1$, logarithmically discretised with $\Lambda = 1.2$.

arbitrary, smooth $J(\omega)$ as they are arising from broadening stick spectra, can be mapped accurately onto chain models.

**Inverse mapping into real space**

The analytic mapping allows a simple inversion $b_x^\dagger = \sum_k U_k(x)a_k^\dagger$ to obtain observables of the original Hamiltonian from the chain observables. For observables which are linear combinations of the creation and annihilation operators, this inverse is straightforward to apply

$$O_x = c_1 b_x + c_2 b_x^\dagger,$$

$$\langle O_x \rangle = \langle \sum_k U_k(x) \left( c_1 a_k + c_2 a_k^\dagger \right) \rangle = \sum_k h(x) \tilde{p}_k(x) \langle c_1 a_k + c_2 a_k^\dagger \rangle,$$  

since it turns numerically, after discretisation of $x$, into a simple matrix multiplication of the form

$$\langle O_x \rangle = U_{xk} \langle c_1 a_k + c_2 a_k^\dagger \rangle.$$  

As an example, in the presented work we used the spin projected displacement

$$f_x^{\uparrow/\downarrow} = \langle \frac{1}{2} \pm \sigma_z b_x^\dagger + b_x \rangle = \sum_{k=0}^{L-2} U_{xk} \text{Re} \left[ \langle \frac{1}{2} \pm \sigma_z a_k^\dagger \rangle \right].$$
Fig. 3.5 The Stieltjes method applied to an oh!mic spectral density with $\alpha = 0.1$ and final chain length $L$. With increasing discretisation points the method converges to the exact analytic result. The oscillatory features are boundary artefacts and vanish as more discretised points are used for the mapping than required by the chain.

Higher order observables such as the occupation $n_x = \hat{b}^\dagger_x \hat{b}_x$ require more careful treatment

$$\langle \hat{b}^\dagger_x \hat{b}_x \rangle = \sum_{k,l=0}^{L-2} U_{xk} U_{xl} \langle \hat{a}^\dagger_k a_l \rangle = U_{xk} \langle \hat{a}^\dagger_k a_l \rangle U^T_{lx},$$  \hspace{1cm} (3.19)

where the full cross correlation $\langle \hat{a}^\dagger_k a_l \rangle$ has to be calculated.

**Mapping of the clustered LVC Hamiltonian**

We can apply the orthogonal polynomial mapping described above to the clustered linear vibronic coupling Hamiltonian Eq. (3.5). This transformation finally leads to the star Hamiltonian

$$\hat{H}_{\text{star}} = \hat{H}_S + \sum_{i=1}^{7} \mathbf{W}_i \| \mathbf{\lambda}_i \| \frac{\langle \hat{a}^\dagger_{i,0} + \hat{a}_{i,0} \rangle}{\sqrt{2}} + \hat{H}_{c,i},$$  \hspace{1cm} (3.20)

$$\hat{H}_{c,i} = \sum_{k=0}^{N_i-1} \epsilon_{i,k} \hat{a}_{i,k}^\dagger \hat{a}_{i,k} + \sum_{k=0}^{N_i-2} t_{i,k} \langle \hat{a}_{i,k}^\dagger \hat{a}_{i,k+1} \rangle + h.c.,$$  \hspace{1cm} (3.21)

with the coupling vector $\mathbf{\lambda}_i = (\lambda_{i,1}, \ldots, \lambda_{i,n})$, containing all couplings of assigned modes, the chain mode frequencies $\epsilon_{i,k}$, and the chain couplings $t_{i,k}$.
This star Hamiltonian model minimises the number of nearest neighbours down to two for all vibrational modes and 7 for the electronic system in the case of DP-Mes (see Fig. 3.3). This is an essential optimisation needed to allow efficient TTNS simulations. Furthermore, the RCs, the modes closest to the system, contain valuable information about the collective action and effect of their respective environment. The RC coupling $\|\lambda_i\|$ and frequency $\epsilon_i,0$ indicate total amount of coupling and weighted average frequency of all represented modes. This allows quick and accurate estimation of time scales and coupling regime. Additionally, expectation values of the RC’s occupation $\langle \hat{n}_i,0 \rangle$ and displacement $\langle \hat{x}_i,0 \rangle$ represent weighted mean values for all constituent modes and can be used as a good proxy for the environment’s collective state. This greatly reduces the number of observables that have to be considered and supports the correlation with observables of the electronic system.

3.2 Matrix Product States and Tree Tensor Networks

Wave functions are the essence of every simulation of quantum systems. Knowing the exact form of the wave function allows the calculation of any observable of a quantum system, meaning we can extract any kind of information available about the system. This is the reason why wave function based methods are considered to be very powerful. However on the downside, the number of parameters defining the wave function grows exponentially with the number of sites, where a site denotes a quantum object such as a quantum harmonic oscillator or a multi-level electronic system. This leads to an exponential memory requirement that makes simulations infeasible, commonly known as the curse of dimensionality. As an example, the combined Hilbert space of a chain of 200 coupled modes, each with a local Hilbert space dimension of 10, has a total dimension of $10^{200}$, while a vector of size 1 GB can store only $6.7 \times 10^7$ parameters.

Matrix product states (MPS) represent a very elegant and efficient way of compressing the wave function in order to reduce the number of free parameters. It works on the principle of disregarding parts of the Hilbert space that are unused, while making them potentially accessible, if necessary. The actual space truncation happens in the space of entanglement, meaning that a well defined MPS can exactly capture any state up to a maximum amount of internal entanglement, as limited by the dimensions of matrices used in the MPS. This means that an MPS with matrix dimensions equal
to 1 can capture all pure product states, equivalent to a mean field theory, while larger dimensions rapidly increase possible inter-site entanglement and the associated Hilbert space. Since matrices can be enlarged dynamically, MPS allows to build an algorithm that automatically adjusts to the transient entanglement properties of the wave function. Thus, we achieve a dynamical truncation of the Hilbert space that optimally follows the wave function. The following outlines the formalism and features of our algorithm, that builds upon the VMPS code written in MATLAB by Cheng Guo, see Ref. [52]. Further details about MPS can be found in Refs. [53, 55, 103].
3.2 Matrix Product States and Tree Tensor Networks

3.2.1 Tensor Basics

The central objects of MPS/TTNS are tensors. In this context, we associate with a tensor a collection of numbers that is stored in a multi-dimensional array. The order of a tensor defines how many dimensions the array has and corresponds to the number of subscript indices. To give a few examples, a 0th order tensor $s$ is a scalar, so just a bare number. A 1st order tensor $v_i$ is a column vector. A 2nd order tensor $M_{ij}$ is a matrix and a 3rd order tensor $T_{ijk}$ can be seen as an object with $k$-many matrices stacked together like pages in a book. In the context of MPS, tensors are diagrammatically represented as rectangles, representing the collection of numbers, with one open leg for each dimension/suffix (see Fig. 3.6). Tensor contractions, the generalisation of the matrix product, are performed by joining tensor legs and setting the same index name. All inner legs which are connecting two tensors, such as $j$ in $A_{ij}B_{jk}$, therefore implicitly invoke a summation as in the Einstein notation.

Other common tensor operations include the permutation of dimensions, such as $A_{ijk} \rightarrow A_{kij}$, which is the higher dimensional analogue of the matrix transpose. Here the indices are names for their respective dimensions, such that a transposition of indices relates to a transposition of the dimensions. In diagrams this can be expressed as a permutation of the legs, but not necessarily, since it does not change the structure of the tensor. Permutations are mostly relevant to change the memory layout of a tensor to prepare it for contractions.

Reshapes change the order of a tensor by joining dimensions together (see Fig. 3.6). A common type of reshaping is the vectorisation of a matrix $M_{ij} \rightarrow M_{(ij)}$, where the parentheses indicate which dimensions are joined into a single dimension. Here it is of special importance to maintain the order of indices since in general $M_{ij} \neq M_{ji}$ and thus $M_{(ij)} \neq M_{(ji)}$.

Permutes and reshapes together can augment any arbitrary tensor contraction into a matrix product. As an example, $\sum_{jmn} A_{ijklmn}B_{pmjno}$ can be performed by first permuting all non-contracted indices to the left and right while simultaneously ordering the dimensions which are to be contracted

$$A_{ijklmn}B_{pmjno} \xrightarrow{permute} A_{ikljmnu}B_{jmnpo}. \quad (3.22)$$

2https://github.com/entron/bosonic-vmps
In the next step a reshape into matrices aligns all contracted dimensions into a single
dimension

$$A_{ikljmn}B_{jmnpo} \xrightarrow{\text{reshape}} A_{(ikl)(jmn)}B_{(jmn)(po)},$$

(3.23)
to yield a simple matrix product $C = AB$ that can be performed highly efficiently
on a CPU with the BLAS routines (Basic Linear Algebra Subprograms), as they are
contained in the Intel Math Kernel Library, for example. In the last step, the result is
reshaped back into tensor form

$$C_{(ikl)(po)} \xrightarrow{\text{reshape}} C_{iklpo}.$$  

(3.24)

A special case of products is the tensor product, commonly denoted as $A \otimes B$, which corresponds to the outer product of the vectorisations of $A$ and $B$ (see Fig. 3.6). This product is commonly used in quantum mechanics to build higher order operators and is employed for the construction of the effective Hamiltonian in Sec. 3.3.2. In MATLAB this is achieved with the Kronecker tensor product

$$O_{ijkl} = A_{ij}B_{kl} = \text{kron}(B_{kl}, A_{ij}),$$

(3.25)

where special care has to be taken with the inverted order. Here we added the indices
to avoid ambiguity in the order of the dimensions.

While it is still feasible to write down a contraction of a linear tensor network,
such as employed in MPS (Sec. 3.2.3), for more complex networks this is not the case.
Therefore, we will mostly work in the diagrammatic description since it is concise and
immediately illustrates which operations are performed.

### 3.2.2 Tensor decomposition

The most important operation in this work is the tensor decomposition by means of a
singular value decomposition (SVD) that allows splitting a large higher order tensor
into two lower order tensors. In combination with truncating dimensions corresponding
to negligible singular values (e.g. $< 10^{-6}$), this technique yields a low-rank tensor
approximation that eliminates the null space across the split.
Tensor decomposition & normalisation:

\[ SVD(\begin{array}{c} Q \end{array}) = \begin{array}{c} U \end{array} S \begin{array}{c} V \end{array} \]
\[ QR(\begin{array}{c} Q \end{array}) = \begin{array}{c} Q \end{array} R \]

\[ \rightarrow r \phi \text{shape} \]

\[ \rightarrow r \phi \text{shape} \]

\[ a \]
\[ b \]
\[ \text{left – normal} \]
\[ \text{mixed} \]
\[ \text{right – normal} \]

Fig. 3.7 Tensor decompositions with SVD and QR in their diagrammatic form and MPS normalisation.
Given an arbitrary higher order tensor $T_{ijklm}$ and a desired splitting into the tuples $(i,k,l), (j,m)$ the decomposition can be performed as

$$T_{ijklm} \xrightarrow{\text{permute}} T_{ikljm}, \quad (3.26)$$

$$T_{ikljm} \xrightarrow{\text{reshape}} T_{(ikl)(jm)}, \quad (3.27)$$

$$T_{(ikl)(jm)} = U_{(ikl)s}S_{s,s}V_{s(jm)}^\dagger, \quad (3.28)$$

where $S$ is a diagonal matrix containing the singular values of this decomposition and thus only involves a sum over its diagonal entries $S_{s,s}$. In a second step the matrices $U$ and $V$ are reshaped into tensors

$$U_{(ikl)s} \xrightarrow{\text{reshape}} U_{ikls}, \quad (3.29)$$

$$V_{(jm)s} \xrightarrow{\text{reshape}} V_{jms}, \quad (3.30)$$

which are of lower order than the original tensor $T$. Although the tensors $U, S,$ and $V$ are now stored as separate objects, they exactly represent the $t$ through their particular product

$$T_{ikljm} = U_{ikls}S_{s,s}V_{s(jm)}^\dagger. \quad (3.31)$$

We call $U, S,$ and $V$ together with their linkage the tensor network for $T$. The matrices $U$ and $V$ contain mutually orthogonal column vectors, as a property of the SVD, and thus are isometries which obey normalisation conditions as depicted in Fig. 3.7. This normalisation is inherited to the resulting tensor network and it is a key property needed to perform the time-evolution with the TDVP scheme (Sec. 3.3).

The singular values of $T$ are commonly sorted in descending order in $S$. If the singular values become negligibly small ($< 10^{-6}$), they can be set to 0, which is equivalent to truncating the corresponding columns in $U$ and $V$. This truncation reduces the size of $U$ and $V$, saving memory, but also introduces an error, such that their contraction is only an approximation to the original tensor $T$. Since the number of non-zero singular values gives the rank of a matrix, truncating negligibly small, but non-zero singular values reduces the rank of the tensor network. This combination of tensor decomposition and truncation of small singular values is the low-rank tensor approximation and the heart of MPS. The best low-rank tensor network approximations to a larger tensor are achieved in case of a decomposition into 3rd order tensors, as presented in the following section.
3.2 Matrix Product States and Tree Tensor Networks

A simpler decomposition of a 3rd order tensor is depicted in Fig. 3.7 together with diagrams explaining the SVD/QR decomposition. The triangular tensors indicate the normalisation condition resulting from the decomposition. The contraction of $U$ across its long edge yields identity (straight line)

$$1 = U^\dagger U, \quad (3.32)$$

while the contraction across the tip of the triangle yields a projector

$$P_U = UU^\dagger, \quad (3.33)$$

onto the range of $U$. In the diagrams, mirroring a tensor either horizontally or vertically usually represents its conjugate transpose, since we work in complex space.

### 3.2.3 Matrix Product States

Matrix product states (MPS) are highly efficient in representing many-body quantum states. In this section we will explain them at the example of a chain of quantum harmonic oscillators (QHO), but the quantum objects can be arbitrary in general.

A single QHO which has eigenstates $|n\rangle$ which form a basis in its Hilbert space $\mathcal{H}$. We can construct a 1D lattice of $L$ QHOs by taking the tensor product of their individual spaces $\mathcal{H} = \mathcal{H}_1 \otimes \cdots \otimes \mathcal{H}_L$. Thus a single product state in this space can be indexed by the individual local basis states $|n_1, \ldots, n_L\rangle$. 
For a 1D lattice of size $L$ with sites $k$ and corresponding local eigenstate basis $|n_k\rangle$ of dimension $d_k$ an arbitrary state of the Hilbert space $|\Psi\rangle \in \mathcal{H}$ can be written as

$$|\Psi\rangle = \sum_{\{n_k\}=1}^{d_k} \Psi_{n_1,\ldots,n_L} |n_1, \ldots, n_L\rangle,$$

where the sum is done over every possible combination of $n_k$. The object containing all probability amplitudes, $\Psi_{n_1,\ldots,n_L}$ is an $L$-th order tensor and can be decomposed with the scheme introduced above. Therefore, any $|\Psi\rangle$ can be written as a matrix product state (MPS) $|\Psi_{MPS}\rangle \in \mathcal{M} \subseteq \mathcal{H}$ via iterative application of singular value decompositions (SVD) on $\Psi_{n_1,\ldots,n_L}$ resulting in the rank-3 tensors $A(k) \in \mathbb{C}^{D_k-1 \times D_k \times d_k}$,

$$|\Psi_{MPS}\rangle = \sum_{\{n_k\}=1}^{d_k} A^{n_1} A^{n_2} \ldots A^{n_L} |n_1, \ldots, n_L\rangle$$

where we have open boundary conditions ($a_0 = a_L = 1$), use the indexing $A_{a_{k-1},a_k}^{n_k} = (A(k))_{a_{k-1},a_k} = (A^{n_k}(k))_{a_{k-1},a_k}$, and allow omitting the site argument for clarity. A diagrammatic representation of this MPS with $L = 5$ is given in Fig. 3.8.

**Bosonic shift**

For bosonic sites the commonly chosen basis (good quantum number) is the occupation $\hat{n}_i$, which determines the dimensions of the MPS matrices to be $D_i \times D_i \times n_i$. Bosonic states with a large displacement $\langle x_i \rangle$, such as coherent states, cause a problem with large occupations $\langle n_i \rangle = \langle x_i \rangle^2$ that require large $d_k$. To prevent the Hilbert space from growing quadratically with $\langle x_i \rangle$, a bosonic shift for each site can be introduced as

$$\delta_i = \langle \Psi | \hat{x} | \Psi \rangle = \langle \Psi | \hat{a}_i + \hat{a}_i^\dagger | \Psi \rangle, \quad (3.36)$$

$$\hat{a}_i^\dagger \rightarrow \hat{a}_i^\dagger + \frac{1}{\sqrt{2}} \delta_i, \quad (3.37)$$

$$\hat{n}_i \rightarrow \hat{n}_i + \frac{\delta_i^2}{2} + \frac{\delta_i}{\sqrt{2}} (\hat{a}_i + \hat{a}_i^\dagger), \quad (3.38)$$

which is equivalent to applying the unitary transformation

$$\hat{T}_i(\delta_i) = e^{-i\hat{p}_i \delta_i} = e^{\frac{\hat{a}_i^\dagger - a_i}{\sqrt{2}}} \delta_i,$$
to the Hamiltonian. Here, in each variational sweep the expectation value for the bosonic displacement $\langle \hat{x}_i \rangle$ is calculated and added to the ladder operators. The performance of the shifting procedure in variational ground state optimisation will be analysed more closely in Sec. 4.3.3. It is in principle also possible to adaptively shift bosons during a time-evolution by applying the shift operator $\hat{T}_i(\delta_i)$ to the Hamiltonian as described above and its adjoint operator $\hat{T}_i(-\delta_i)$ to the MPS, but we have not yet explored this direction.

**Optimised boson basis**

If the local Hilbert space dimensions $d_k$ are very large, as for QHOs, we can employ an optimised boson basis (OBB), as introduced by Guo et al. [53], which is realized via an additional map (isometry) $V \in \mathbb{C}^{d_k \times d_{OBB,k}}$ from the optimized basis $|\tilde{n}_k\rangle$ into the local basis $|n_k\rangle$

$$A_{n_{k-1},a_k}^{n_{k},\tilde{n}_k} = \sum_{\tilde{n}_k=1}^{d_{OBB,k}} \tilde{A}_{n_{k-1},a_k}^{n_{k},\tilde{n}_k} V_{n_k,\tilde{n}_k},$$

(3.40)

where we will write $A$ instead of $\tilde{A}$ throughout this work (see Fig. 3.8). This mapping allows high compression ($d_{OBB,k} \ll d_k$) of the local oscillator basis in the case of large variances $\text{Var}(n_k)$, which has been shown to be highly effective in dealing with quantum-critical SBMs [53]. The Hilbert space compression via $V$ can substantially improve the performance of simulations as demonstrated in Fig. 3.14. This technique is more general than the bosonic shift and can be combined with it.

**Adaptive tensor expansion and truncation**

The efficiency of MPS is based on low-rank tensor approximations which significantly reduce the number of variational parameters in the tensors $A(k), V(k)$. This restricts the Hilbert space spanned by the MPS to a manifold $\mathcal{M} \subset \mathcal{H}$. The combination of high truncation and dynamical “on the fly” bond adjustment, while representing an optimal manifold, allows the implementation of an efficient variational algorithm with significant advantages for computational speed and accuracy [53, 103, 136]. We truncate and expand the bonds $a_k$ and $\tilde{n}_k$ such that the smallest singular values kept are within $10^{-6}$ and $10^{-8}$ leading to adaptive dimensions $D_k$ and $d_{OBB,k}$ with upper bounds $D_{\text{max}}$ and $d_{OBB,\text{max}}$. The upper bounds are necessary to prevent the algorithm from taking more memory than is available on the machine, or to allow faster but less accurate simulations. In turn this means that the singular values can also have values
well above $10^{-6}$ which creates a higher approximation error. The truncation thresholds around $10^{-6}$ are chosen since the singular values correspond to probability amplitudes of the Schmidt decomposition. Since an amplitude of $10^{-6}$ corresponds to an error in probability of $10^{-12}$ we can safely truncate smaller values. To avoid frequent memory reallocations we truncate all singular values below $10^{-8}$, while keeping at least one singular value below $10^{-6}$. In this light, even a threshold at $10^{-2}$ can be sufficiently accurate if overall errors on the scale of $1 - 2\%$ are acceptable.

### 3.2.4 Variational ground state optimization

Once we represented a state as an MPS, any variational ground state optimization and time evolution can be performed iteratively on the individual tensors by sweeping along the chain. During the sweeping procedure we keep the state in a mixed canonical form to make use of orthogonality conditions (see Fig. 3.7). Furthermore only one matrix can be focused (centred), which means its vectorization $v$ has unit length $\langle v|v \rangle = 1 = \langle \Psi_{MPS}|\Psi_{MPS} \rangle$. Figure 3.9 diagrammatically explains all normalizations of $A$ and the possible centre matrices $A_C(k), V_C(k)$ and bond centres $C_a(k), C_{\bar{n}}(k)$ which have special relevance for the time-evolution explained later. When focusing on site $k$, all $A$ matrices of site $i < k$ will be kept left-orthonormal while matrices $i > k$ will be right-normalized to produce orthonormal left and right basis states $|\Phi_L\rangle, |\Phi_R\rangle$ (see
The ground state is found variationally by minimising the energy given by the time independent Schrödinger equation

$$H |\Psi\rangle = E |\Psi\rangle .$$ (3.42)

A tensor $A(k)$ of the MPS is optimised by minimising the energy while keeping all other tensors of the constant. This can be achieved by constructing the effective Hamiltonian $H(k)$ for tensor $A(k)$ (see Fig. 3.13), which incorporates all tensors that are kept constant. The most optimal parameters for $A(k)$ are then found by finding the eigenvector corresponding to the lowest eigenvalue of $H(k)$. The search for only the lowest eigenvalue and its corresponding eigenstate can be efficiently done with the Arnoldi iteration, started from the previous parameters in $A(k)$, which avoids a complete diagonalisation.

After updating $A(k)$ the focus is carried to the next site. A single sweep consist of optimising all tensors ($A$ and $V$) by sweeping through the chain from left to right and back. Depending on the particular Hamiltonian, it can be more favourable for the convergence to only optimise by sweeping into one direction, as is the case for a chain obtained after a logarithmic discretisation.

Between the sweeps, depending on various criteria, the MPS can be truncated or expanded with the methods described above to increase either speed or accuracy. The convergence criterion of the optimization is a maximum deviation of $5 \times 10^{-15}$ of the ground state energy within one sweep. A very detailed description can be found in a review by Ulrich Schollwöck [103] and in Ref. [85].

### 3.2.5 Tree Tensor Network States

Matrix product states are optimal for 1D chain Hamiltonians, as they can optimally capture the arising short-range entanglement. Nevertheless, only models with up to 2 environments can be put into a chain form with the system in the middle. As soon as more than 2 environments are required, the Hamiltonian assumes a star topology with the system at its centre (see Fig. 3.3). Following the MPS principle, the optimal tensor network for $\hat{H}_{star}$ assumes the same star structure as the Hamiltonian.
In particular, we shape the MPS such that each tensor represents one physical (local) site of $\hat{H}_{\text{star}}$. The tensor connections follow the coupling structure in $\hat{H}_{\text{star}}$ to minimise inter-site entanglement, giving a star-MPS which is a special form of a tree tensor network state (TTNS). Since the central tensor (Fig. 3.10 left) connecting the system with all seven environments (in this example) grows rapidly with increasing bond dimension ($D^7$), we decompose it into a tree-network of six smaller entanglement renormalisation tensors (ER-tensors), as described in the following section.

The main property of TTNS is that it is the most general 1D tensor network, since a tree does not contain any closed loops in contrast to 2D tensor networks. This is crucial for a well-defined tensor network normalisation, as is needed for the TDVP (Sec. 3.3). Although a TTNS might seem more complex than an MPS, all concepts described above can be generalised and applied in the same way to higher order tensors.

As mentioned earlier, we will withhold from writing mathematical expressions for the TTNS, since it would only add unnecessary complexity. A particular difficulty is the indexing of the tensors, based on their location in the TTNS, and a corresponding labelling of the bonds, such that everything can be expressed in a single equation. While this issue is not present in the sketches, they can additionally give faster, more intuitive insight into the connectivity and layout of the TTNS.

### 3.2.6 Entanglement Renormalisation Tensors

In higher order tensors connecting multiple subsystems, such as environment chains, entanglement between the subsystems can be harnessed to reduce tensor dimensions. As an example, if two systems $A$ and $B$ with entropies $S_A$ and $S_B$ are not entangled, the entropy of their combined system is equal to the sum

$$S_{AB} = S_A + S_B. \tag{3.43}$$

If instead $A$ and $B$ are entangled, then the overall entropy $S_{AB}$ obeys

$$|S_A - S_B| \leq S_{AB} < S_A + S_B, \tag{3.44}$$

where $S_{AB}$ is minimal for maximum entanglement.

Transferring this insight to the case of multiple entangled subsystems, all connected through a single higher order tensor, we can expect large memory savings if we apply an appropriate system combination scheme that effectively decomposes the central tensor.
while retaining the most relevant effective states. We can achieve this by replacing the central tensor with an equivalent network of 3rd order tensors. Each of these auxiliary entanglement renormalisation (ER) tensors then encodes how two incoming subsystems are combined and rotated into a minimal effective basis set and then connected to the rest of the network. Since tensor bond dimensions scale proportionally to the entropy they have to represent, an optimal decomposition scheme minimises the entropy on each bond of the tensor network. Therefore, it is crucial to find pairings of subsystems that yield a network with lower entropy which is fulfilled by strongly entangled subsystems.

The optimal network structure is determined by analysing the entanglement within the original core tensor in a preceding, expensive star-MPS calculation. The key insight is that although this calculation of the star-MPS network with small $D \in [5, 10]$ is highly inaccurate, the centre tensor still exhibits the major entanglement structure between the subsystems. As shown in Fig. 3.10, calculating the entanglement entropy for all possible decompositions of this tensor can yield insights about its entanglement structure (blue lines).
Fig. 3.11 (a-c) All possible decompositions of a tensor connecting subsystems $A, B, C, D$. The numbers in the tensors indicate the amount of entropy saved through each combination. Splitting (a) is most optimal with the lowest entropy $S_{AD} = S_{BC} = 2.46$, although $B$ and $C$ are only weakly entangled.

While by intuition, prioritising the combination of highly entangled environments should be most optimal, there are constellations where this is not the case. This is best illustrated by Fig. 3.11, which is derived from an actual calculation of DP-Mes. In this example, $A, B,$ and $C$ are outer legs (environments) of the centre tensor, while $D$ is an inner bond towards another ER tensor. As seen from the entropy reduction between outer legs, $A$ and $B$ have the strongest entanglement with a relative entropy reduction of 19.5%, followed by $A$ and $C$ (12.6%), and $B$ and $C$ (7%). But the corresponding decomposition yields a large combined entropy $S_{AB} = 2.72$ rendering decomposition scheme 3 relatively inefficient. The reason is the even stronger entanglement between $A$ and the inner leg $D$, which if treated as an environment, yields an even larger entropy reduction of 48% in decomposition a.

Figure 3.12 gives examples for different possible ER-networks for DP-Mes, based on a star MPS calculation. While the right network was obtained by searching for the best bipartition into two sets of legs, the left network was found for an optimal partition into three sets. In the right network, the inner entropies give a total of 12.17 and the environments of similar irrep are combined first, which agrees with intuition. The left network instead gives faster simulations at similar accuracy. It has a lower maximum entropy of 2.85 but a larger total inner entropy of 12.5 and combines the environments less regular.

This above examples should show, that it is not straightforward to define the properties of an optimal decomposition. It seems most advantageous to minimise the largest occurring entropy to achieve a better compression. Knowledge about the underlying model symmetries and how they relate to each other, such as split environments $A_1$ and $B_1$ can help to find a good decomposition, but they can also lead into the wrong direction as seen at $B_2$. Thus an optimal decomposition is found best and quickest with an objective path-finding algorithm.
Fig. 3.12 Two possible ER decompositions of a star MPS centre tensor along with resulting entanglement entropies along the bonds. While both networks give similar dynamics, the left is more optimal since its maximum entropies are 2.85 and 2.72, while the right network has 2.97 and 2.72.
Regarding space complexity, the final ER-network turns the initial exponential scaling $O(D^N)$ into a linear scaling $O(ND^3)$ in the number of environments. For comparison, while in the star MPS without ER-nodes we can reasonably simulate with up to $D \in [5, 10]$ between the system and each environment, in the TTNS we can use $D_{Node} \in [50, 80]$ while still gaining a speed-up and higher accuracy (see Sec. 3.3.6). Therefore, this is a key technique to enable efficient simulation for $>3$ environment models with high accuracy.

### 3.3 Time-dependent variational principle

The time evolution is performed with the time-dependent variational principle (TDVP) described in Refs. [55, 75]. It is derived from the Dirac-Frenkel variational principle and obtained by projecting the Schrödinger equation onto the tangent space of the MPS manifold $\mathcal{M}$ to find optimal equations of motion for each MPS centre tensor within $\mathcal{M}$ to generate the best approximation $|\Psi_{MPS}(t)\rangle$ to the exact state $|\Psi(t)\rangle$. Haegeman et al. have shown that this is equivalent to a Lie-Trotter splitting of the MPS instead of the time-evolution operator $U(t) = e^{-i\hat{H}t}$. Unlike the Suzuki-Trotter splitting of $U(t)$, errors only accrue from the integration scheme.

Since the OBB modifies the MPS network, our implementation of the TDVP needed an extension of the original TDVP scheme. To prove that this can be done and to derive the appropriate integration scheme, we will present in Sec. 3.3.1 the derivation of the tangent space projector $\hat{P}_{T_{\Psi_{MPS}}, \mathcal{M}}$ in the formalism established by Ref. [75]. Additionally we will give a more simplified description of the resulting integration scheme in Sec. 3.3.2. Without further proof we will use the gained insights to further generalise the TDVP to arbitrary TTNS in Sec. 3.3.3. Afterwards we give an overview how the time-evolution can be performed numerically using Krylov subspace techniques in Sec. 3.3.4. Since the time-evolution of a star-MPS can be very demanding and challenging, we introduce an additional Trotter splitting of the time-evolution for higher order tensors in Sec. 3.3.5.

#### 3.3.1 Derivation of the tangent space projector

This derivation will be similar to Theorem 3.1 of Ref [75] but using the left canonical form of the MPS with OBB matrices. To be more consistent with their notation and
for clarity, we will use \( n_k, \tilde{n}_k \) and \( a_k \) instead of \( d_k, d_{OBB,k} \) and \( D_k \) to address bond dimensions.

Additionally to the definitions of Lubich et al. we need to introduce further notation to address the components of an MPS tensor \( X \in \mathbb{R}^{n_1 \times \cdots \times n_L} \) and their unfoldings (as depicted in Fig. 3.9).

Any site tensor \( C_k \in \mathbb{R}^{a_{k-1} \times n_k \times a_k} \) can be written as a matrix using the left and right unfolding \( \mathbf{C}_k^< \in \mathbb{R}^{(a_{k-1}, n_k) \times a_k} \) and \( \mathbf{C}_k^> \in \mathbb{R}^{(a_k, n_k) \times a_{k-1}} \). Similarly the orthonormalised site tensors \( \mathbf{Q}_k^<, \mathbf{Q}_k^> \in \mathbb{R}^{a_{k-1} \times n_k \times a_k} \) are unfolded as

\[
\mathbf{Q}_k^< \in \mathbb{R}^{(a_{k-1}, n_k) \times a_k},
\]

\[
\mathbf{Q}_k^> \in \mathbb{R}^{(a_k, n_k) \times a_{k-1}},
\]

and additionally fulfil the normalization conditions \( \mathbf{Q}_k^< \mathbf{Q}_k^T \mathbf{Q}_k^< = 1_{a_k} \) and \( \mathbf{Q}_k^> \mathbf{Q}_k^T \mathbf{Q}_k^> = 1_{a_{k-1}} \).

Unfolded segments of the MPS to the left and right of site \( k \) are denoted as \( \mathbf{X}_{\leq k-1} \in \mathbb{R}^{(n_1 \cdots n_{k-1}) \times a_{k-1}} \) and \( \mathbf{X}_{\geq k+1} \in \mathbb{R}^{(n_{k+1} \cdots n_L) \times a_k} \), respectively. If these parts are left and right orthonormalised we will write \( \mathbf{Q}_{\leq k-1} \) and \( \mathbf{Q}_{\geq k+1} \).

This notation can be transferred to the OBB tensors \( \mathbf{A}_k \in \mathbb{R}^{a_{k-1} \times \tilde{n}_k \times a_k} \) and \( \mathbf{V}_k \in \mathbb{R}^{n_k \times \tilde{n}_k} \) forming a decomposition of the site tensors \( \mathbf{C}_k \) as

\[
\mathbf{C}_k^< = \left( \mathbf{V}_k \otimes \mathbf{1}_{a_{k-1}} \right) \mathbf{A}_k^<.
\]

The OBB tensors can also be orthonormalised, denoted as \( \mathbf{Q}_{A,k} \) and \( \mathbf{Q}_{V,k} \in \mathbb{R}^{n_k \times \tilde{n}_k} \), where \( \mathbf{Q}_{V,k}^T \mathbf{Q}_{V,k} = \mathbf{Q}_{A,k}^T \mathbf{Q}_{A,k} = 1_{\tilde{n}_k} \). They compose \( \mathbf{Q}_k^< \) and \( \mathbf{Q}_k^> \) as:

\[
\mathbf{Q}_k^< = \left( \mathbf{Q}_{V,k} \otimes \mathbf{1}_{a_{k-1}} \right) \mathbf{Q}_{A,k}^<,
\]

\[
\mathbf{Q}_k^> = \left( \mathbf{Q}_{V,k} \otimes \mathbf{1}_{a_k} \right) \mathbf{Q}_{A,k}^>.
\]

Furthermore it is necessary to define an new unfolding \( \tilde{\mathbf{Q}}_k^< \in \mathbb{R}^{(a_{k-1}, a_k) \times \tilde{n}_k} \) to support the following notation.

Let \( X^{Tk} \) be the \( k \)th tensor transpose cycling the \( k \)th tensor dimension of \( X \) to the first position while keeping the order of all other dimensions. This permutation can be written as

\[
X(i_1, i_2, \ldots, i_L) = X^{Tk}(i_{\sigma_k(1)}, i_{\sigma_k(2)}, \ldots, i_{\sigma_k(L)}),
\]

with the \( k \)-cycle \( \sigma_k = (k \ 1 \ 2 \ \cdots \ k-1) \in \Sigma_L \). The inverse of this transpose is \( X^{T_{-k}} \) defined by the \( k \)-cycle \( \sigma_{-k} = \sigma_k^{-1} = (k \ k-1 \ \cdots \ 2 \ 1) \). The \( k \)th unfolding
Computational Methods

\( X^{(k)} \) of \( X \) denoted with round braces is then equivalent to the first unfolding of the \( k \)th tensor transpose of \( X \),

\[
X^{(k)} = X^{T_k(1)} \in \mathbb{R}^{n_k \times (n_1 \ldots n_{k-1} n_{k+1} \ldots n_L)},
\]

\[
X = \text{Ten}_{(k)} \left[ X^{(k)} \right] = \text{Ten}_1 \left[ X^{T_k(1)} \right]^{T-k},
\]  

(3.49)

with the corresponding tensor reconstruction as its inverse.

A matrix \( A \in \mathbb{R}^{m \times n}, m > n \) with \( \text{rank}(A) = n \) has a left inverse

\[
A^{-1} = \left( A^T A \right)^{-1} A^T,
\]

\[
A^{-1} A = I_n,
\]  

(3.50)

and a projector \( P_A \) onto the range of \( A \)

\[
P_A = A A^{-1},
\]  

(3.51)

which will be used for the definition of the tangent space projector.

The tangent space \( T_X \mathcal{M} \) of any state \( X \in \mathcal{M} \) of the OBB-MPS manifold can be constructed from the orthogonal subspaces \( \mathcal{V}_{A,k}, \mathcal{V}_{V,k} \). We will use the MPS in the left canonical gauge including site \( k \),

\[
X = \text{Ten}_k \left[ (Q_{V,k} \otimes Q_{\leq k-1}) \delta Q_{A,k}^T X_{\geq k+1}^T \right].
\]  

(3.52)

Thus we have

\[
\mathcal{V}_{A,k} = \left\{ \text{Ten}_k \left[ (Q_{V,k} \otimes Q_{\leq k-1}) \delta Q_{A,k}^T X_{\geq k+1}^T \right] : \delta Q_{A,k}^T \delta Q_{A,k}^T = 0 \text{ for } k \neq L \right\},
\]

\[
\mathcal{V}_{V,k} = \left\{ \text{Ten}_{(k)} \left[ \delta Q_{V,k} (Q_{A,k}^T)^T (X_{\geq k+1} \otimes Q_{\leq k-1})^T \right] : \delta Q_{V,k} \in \mathbb{R}^{n_k \times \tilde{n}_k}, \right. \]

\[
\left. Q_{V,k}^T \delta Q_{V,k} = 0 \right\},
\]  

(3.53)

(3.54)

with \( X^T \geq L + 1 = 1 \) since \( a_L = 1 \). Since these subspaces are mutually disjoint, the tangent space is

\[
T_X \mathcal{M} = \bigoplus_{k=1}^L (\mathcal{V}_{A,k} \oplus \mathcal{V}_{V,k}),
\]  

(3.55)
and allows the decomposition of any tangent vector \( \delta X \in T_X \mathcal{M} \)

\[
\delta X = \sum_{k=1}^{L} (\delta X_{A,k} + \delta X_{V,k}),
\]

\[
\langle \delta X_{i,k}, \delta X_{j,l} \rangle = 0 \quad \text{for } i \neq j, k \neq l.
\]

We want to find the tangent space projector \( P_{TX,M} \) for an arbitrary \( Z \in \mathbb{R}^{n_1 \times \cdots \times n_L} \) such that the projection \( \delta U = P_{TX,M}(Z) \in T_X \mathcal{M} \) is orthogonal and therefore satisfies

\[
\langle \delta U, \delta X \rangle = \langle Z, \delta X \rangle \quad \forall \delta X \in T_X \mathcal{M}.
\]

Due to the disjoint subspaces \( \mathcal{V}_{i,k} \) we can decompose

\[
\delta U = \sum_{k=1}^{L} (\delta U_{A,k} + \delta U_{V,k}),
\]

with \( \delta U_{i,k} \in \mathcal{V}_{i,k} \) and find

\[
\langle \delta U_{i,k}, \delta X_{i,k} \rangle = \langle Z, \delta X_{i,k} \rangle,
\]

for \( i \in \{A,V\} \). The projection is then defined by the \( \delta B \) matrices in

\[
\delta U^{(k)}_{A,k} = (Q_{V,k} \otimes Q_{\leq k-1}) \delta B^{\leq}_{A,k} X_{\geq k+1}^T,
\]

\[
\delta U^{(k)}_{V,k} = \delta B_{V,k} (\hat{Q}^{\leq A,k})^T (X_{\geq k+1} \otimes Q_{\leq k-1})^T,
\]

with \( Q_{A,k}^{\leq T} \delta B_{A,k} = 0 \) for \( k \neq L \) and \( Q_{V,k}^{T} \delta B_{V,k} = 0 \).

To find expressions for \( \delta B_{A,k} \) and \( \delta B_{V,k} \) we follow the same steps as Ref. [75]. Here we give an outline for \( \delta B_{V,k} \) to obtain \( \delta U^{(k)}_{V,k} \). First substitute the expressions for \( \delta U^{(k)}_{V,k} \) and \( \delta X^{(k)}_{V,k} \) (Eq. (3.54)) into Eq. (3.59) and isolate the term \( \delta Q_{V,k} \) in both inner products:

\[
\langle \delta U^{(k)}_{V,k}, \delta X^{(k)}_{V,k} \rangle = \langle \delta B_{V,k} M^T, \delta Q_{V,k} M^T \rangle = \langle \delta B_{V,k} M^T M, \delta Q_{V,k} \rangle,
\]

\[
\langle Z^{(k)}, \delta X^{(k)}_{V,k} \rangle = \langle Z^{(k)} M, \delta Q_{V,k} \rangle,
\]

where we defined \( M = (X_{\geq k+1} \otimes Q_{\leq k-1})\hat{Q}^{\geq A,k} \) for clarity. To remove the inner products on both sides we use the property \( \langle A, C \rangle = \langle B, C \rangle \rightarrow P_{C} A = P_{C} B \) with
$P_{\delta Q_{V,k}} = \mathbb{I}_{n_k} - P_{V,k}$ and then substitute the found expression for $\delta B_{V,k}$ into $\delta U^{(k)}_{V,k}$:

$$
\delta B_{V,k} = (\mathbb{I}_{n_k} - P_{V,k}) Z^{(k)} M (M^T M)^{-1},
\delta U^{(k)}_{V,k} = (\mathbb{I}_{n_k} - P_{V,k}) Z^{(k)} (MM^{-1}),
$$

(3.62)

Thus we derived the projection of $Z$ onto the tangent space as

$$
\delta U^{(k)}_{V,k} = \left( \frac{1}{\mathbb{I}_{n_k} - P_{V,k}} \right) Z^{(k)} \big( M M^{-1} \big),
\delta U^{(k)}_{V,k} = \left( \frac{1}{\mathbb{I}_{n_k} - P_{V,k}} \right) Z^{(k)} P_M.
$$

(3.63)

where we used the projectors

$$
P_{V,k} = Q_{V,k} Q_{V,k}^T,
P_{\leq k-1} = Q_{\leq k-1} Q_{\leq k-1}^T,
P_{\geq k+1} = X_{\geq k+1} X_{\geq k+1}^{-1} = Q_{\geq k+1} Q_{\geq k+1}^T.
$$

(3.64)

In the notation of Ref. [55] the tangent space projector thus reads

$$
\hat{P}_{T_{\Psi_{MPS}}}^{[k,M]} = \sum_{k=1}^{L} \hat{P}_{L}^{[1:k-1]} \otimes \hat{P}_{V}^{[k]} \otimes \hat{P}_{R}^{[k+1:L]}
- \sum_{k=1}^{L-1} \hat{P}_{L}^{[1:k]} \otimes \hat{P}_{R}^{[k+1:L]},
+ \sum_{k=1}^{L} \hat{P}_{A}^{[1:k-1,k+1:L]} \otimes (\mathbb{I}_{k} - \hat{P}_{V}^{[k]}).
$$

(3.65)

with the left and right chain projectors

$$
\hat{P}_{L}^{[1:k]} = \sum_{a_k=1}^{D_k} |\Phi_{L,a_k}^{[1:k]} \rangle \langle \Phi_{L,a_k}^{[1:k]}|,
\hat{P}_{R}^{[k+1:L]} = \sum_{a_k=1}^{D_k} |\Phi_{R,a_k}^{[k+1:L]} \rangle \langle \Phi_{R,a_k}^{[k+1:L]}|,
\hat{P}_{V}^{[k]} = \sum_{\tilde{n}_k=1}^{d_{OBB,k}} |\Phi_{\tilde{n}_k}^{[k]} \rangle \langle \Phi_{\tilde{n}_k}^{[k]}|,
\hat{P}_{A}^{[1:k-1,k+1:L]} = \sum_{\tilde{n}_k=1}^{d_{OBB,k}} |\Phi_{A,\tilde{n}_k}^{[1:k-1,k+1:L]} \rangle \langle \Phi_{A,\tilde{n}_k}^{[1:k-1,k+1:L]}|,
$$

(3.66)
Using these expressions to project $H \ket{\Psi_{MPS}}$ onto $T\ket{\Psi_{MPS}} \mathcal{M}$ we get, after a Lie-Trotter decomposition of the MPS, a system of equations of motion for each MPS tensor $V_C(k)$ and $A_C(k)$ as well as for the bond matrices $C_\bar{n}(k)$ and $C_a(k)$ which can be solved directly by

$$V_C(k,t) = e^{-iH_V(k)t}V_C(k,0),$$
$$C_\bar{n}(k,t) = e^{+iH_\bar{n}(k)t}C_\bar{n}(k,0),$$
$$A_C(k,t) = e^{-iH_A(k)t}A_C(k,0),$$
$$C_a(k,t) = e^{+iH_a(k)t}C_a(k,0).$$

The effective local Hamiltonians of each tensor used in the exponentials are obtained by a full contraction of the Hamiltonian with the MPS, while omitting the respective tensor. A diagrammatic representation is given in Fig. 3.13.

### 3.3.2 1-tensor update scheme: MPS with OBB

A key formal result we present is this new OBB-TDVP scheme with a single-tensor update, which is given by

$$V_C(k,t + \Delta t) = e^{-iH_V(k)\Delta t}V_C(k,t),$$
$$\downarrow \text{SVD}$$
$$C_\bar{n}(k,t) = e^{+iH_\bar{n}(k)\Delta t}C_\bar{n}(k,t + \Delta t),$$
$$\downarrow \text{SVD}$$
$$A_C(k,t + \Delta t) = e^{-iH_A(k)\Delta t}A_C(k,t),$$
$$\downarrow \text{SVD}$$
$$C_a(k,t) = e^{+iH_a(k)\Delta t}C_a(k,t + \Delta t),$$

where bold notation indicates vectorizations of the tensors. The effective local Hamiltonian $H_\sim(k)$ generating the optimal time evolution of a centre matrix is obtained by full contraction with all MPS matrices except for the to be evolved centre matrix as depicted in Fig. 3.13. This scheme can be seen to maintain the general form of the TDVP equations given in Refs. [55, 75]. Essentially, after each forward evolution $t \rightarrow t + \Delta t$ of a centred tensor $V_C$ or $A_C$, the centred bond matrix $C_{\bar{n}/a}(t + \Delta t)$ obtained via SVD has to be evolved backwards in time $t + \Delta t \rightarrow t$ before contraction with the next tensor. By sweeping left-to-right and back to the left with a time step $\Delta t/2$ one
Fig. 3.13 All effective local Hamiltonians needed for the TDVP with OBB.
obtains a second order symmetric integrator with error of order $O(\Delta t^3)$. Since for each evolution step the entire effective Hamiltonian is applied, it is possible to include long-range interactions.

The single-tensor update with OBB has significant advantages over the 1-site update TDVP without OBB in cases where a large number of local states has to be considered. The two additional evolution steps for $V_C$ and $C_n$ can outweigh the unfavourable scaling of the 1-site TDVP without OBB. The computational complexity of the TDVP with OBB scales as $O(\max(D^3d_OBB, D^2d_OBB^2, d_OBBd_OBB^2))$ which is significantly faster than the original scaling $O(\max(D^3d, D^2d^2))$ without OBB for $d_OBB \ll d$. The scaling behaviour of OBB-TDVP is also more preferable in comparison with the common time-evolving block decimation (TEBD) ($O(d^3D^3)$) and the very recently proposed TEBD with local basis optimization (TEBD-LBO) of Brockt et al. \[18\] with a scaling of $O(\max(d_OBB^3D^3, d_OBB^3D^2))$. The latter uses a technique very similar to the OBB to map the local Hilbert space onto an optimized basis to reduce the computational effort. The main difference that makes TDVP much faster than TEBD is that TDVP is a 1-site update scheme that involves operations on only small tensors, while the TEBD is a 2-site integrator which contracts two neighbouring sites to produce one large tensor, which gets split into two separate tensors in a subsequent step.

As evident from the example given in Fig. 3.14 it is possible to increase the local Hilbert space on each site from $d_k = 200$ to $d_k = 500$ at no extra cost by introducing an OBB of $d_OBB = 65$. Similarly a calculation needing $d_k = 500$ can be accelerated by a factor of 4-10 by using an OBB, depending on the amount of (allowed) entanglement. Generally, the smaller $d_OBB$, the less entanglement can be captured by the MPS between a site and its left and right environment, but the faster and more memory efficient is the computation.

### 3.3.3 1-tensor update scheme: TTNS

Although the TTNS seems to consist of functionally different components (ER-tensors, MPS chains, OBB matrices), we can identify them as nodes having one parent and multiple child tensors. Since the quasi 1D structure of the tree ensures correct TTNS normalisation we can use the insights from Ref. \[104\] and generalise it to nodes with more than one child. We recursively define the time-evolution of a single node as presented in Algorithm 1, where we denote $C$ the centre matrix obtained by SVD, $ttns$ is the TTNS object of the (sub-)tree, $ttns.node$ is the current root tensor of
Algorithm 1 TDVP for TTNS

1: function EVOLVE_SUBTREE(ttns, dt) ▷ TDVP of Subtree
2:     EVOLVE(ttns.node, dt/2)
3:     for i = 1 : N_child do ▷ iterate through child nodes
4:         EVOLVE_CHILD(ttns, dt, i)
5:     end for
6:     EVOLVE(ttns.node, dt/2)
7: end function

8: function EVOLVE_CHILD(ttns, dt, i) ▷ TDVP of Subtree
9:     C ← SVD_TO_CHILD(ttns.node, i)
10:    EVOLVE(C, −dt/2) ▷ evolve back in time
11:    CONTRACT(C, ttns.child(i))
12:    EVOLVE_SUBTREE(ttns.child(i), dt)
13:     C ← SVD_FROM_CHILD(ttns.child(i))
14:    EVOLVE(C, −dt/2)
15:    CONTRACT(C, ttns.node)
16: end function
3.3 Time-dependent variational principle

Fig. 3.15 Possible integration techniques to perform the action of a matrix exponential on a vector.

the (sub-)tree, and $ttns.child$ is an array of references to all child sub-trees. Starting this recursive scheme from the root node with a pre-defined ordering of child nodes constitutes a sweep. To obtain a symmetric second-order integrator with error of order $O(\Delta t^3)$, we sweep through the tree such that each tensor is updated twice by a time step of $\Delta t/2$.

The effective Hamiltonians needed for the time-evolution of a node, within the $\text{evolve()}$ statements, are obtained in a very similar way as for the propagation of a chain tensor, by contracting the Hamiltonian with all tensors which are not being propagated in the current update (see Fig. 3.13). This algorithm generalises and applies very naturally to ER-tensors since they can also be seen as time-dependent tensors for which we can calculate an effective Hamiltonian. The only difference is that the ER-tensors do not have an own local Hilbert space and that the coupling terms between system and chains have to be carried forward very similar to long-range couplings, which is the reason why TDVP is especially well suited for the evolution of ER-tensors.

Finally, this scheme can also be applied recursively to any tree tensor network with more layers. This allows in principle the simulation of arbitrary Hamiltonians which are representable as a tree without loops.
### 3.3.4 Numeric integration with Krylov subspace technique

The matrix exponential of an operator $H_{\text{eff}} \in \mathbb{C}^{n \times n}$, as needed for TDVP, can be performed in several ways (see Fig. 3.15 and Ref. [82]). In the simplest approach, the operator can be taken explicitly, in the form of a matrix and exponentiated with the MATLAB routine `expm` to be subsequently applied to the vectorised tensor. This function internally uses a scaling and squaring algorithm with a Padé approximation to estimate the matrix exponential. It turns out to be very fast for small operators $n < 100$ but scales badly for larger $n$.

Building upon this implementation we also used the Krylov subspace integrator EXPOKIT [109] with the explicit $H_{\text{eff}}$. This method efficiently compresses $H_{\text{eff}}$ by building the most relevant basis $V_m$ of the $m$-dimensional Krylov subspace $K_m$ around the to be time-evolved vector $A$

$$K_m = \text{span}\{A, H_{\text{eff}}A, \ldots, (H_{\text{eff}})^{m-1}A\}.$$  \hfill (3.68)

Usually, we choose the size $m$ of this basis to be much lower than $n$, such that the transformation

$$H = V_m^\dagger H_{\text{eff}} V_m,$$  \hfill (3.69)

yields an $m \times m$ operator that can be exponentiated efficiently with `expm` and transformed back to be subsequently applied to the vector $A$. Since our operator is always hermitian, we modified the Krylov integrator to create the basis of the Krylov subspace with the computationally more efficient Lanczos algorithm instead of the previously implemented Arnoldi iteration (see Sec. 3.A). This method gains a better scaling than `expm` but is still inefficient for large $n$ since it makes use of the full explicit operator $H_{\text{eff}}$.

The large $n$ scaling behaviour can be improved by only implicitly constructing $H_{\text{eff}}$ which never actually constructs the matrix. Here we replace the matrix $H_{\text{eff}}$ by a function $f$ that returns the same output

$$f(A) = H_{\text{eff}}A,$$  \hfill (3.70)

but internally contracts the tensor $A$ with the individual components that are contained in $H_{\text{eff}}$ in an optimal order. This massively reduces memory use, but creates overhead for small $n$. The benchmarks in Fig. 3.16 exhibit the improved scaling behaviour for $n > 250$. To allow passing $f$ to EXPOKIT, the norm estimation of the operator is
3.3 Time-dependent variational principle

Fig. 3.16 CPU time taken for the matrix exponential of operators with different sizes. The implicit Krylov integration is only faster for operators larger than $250 \times 250$.

\begin{align*}
e^{-iH_{\text{eff}}\Delta t} A &= e^{-iH_{\text{eff}}\Delta t} \quad \rightarrow \quad e^{-iH_{\text{eff}}\Delta t} \quad \rightarrow \quad e^{-iH_{\text{eff}}\Delta t} \quad \rightarrow \quad e^{-iH_{\text{eff}}\Delta t} \\
&= e^{-iH_{\text{eff}}\Delta t} \quad \rightarrow \quad e^{-iH_{\text{eff}}\Delta t} \quad \rightarrow \quad e^{-iH_{\text{eff}}\Delta t} \quad \rightarrow \quad e^{-iH_{\text{eff}}\Delta t}
\end{align*}

Fig. 3.17 Trotter splitting of $H_{\text{eff}}$ combined with QR decompositions of the tensor $A$. The numbers 1-3 above the legs label the child environments while 0 represents the leg to the parent node.

performed on the transformed $H$ since its norm is similar to the norm of $H_{\text{eff}}$, at least in the relevant subspace. This is of particular importance since the operator norm is necessary to estimate the error of the integration and to derive an optimal time step.

The thresholds used to determine the choice of integrator based on size $n$ of $H_{\text{eff}}$ are dependent on the computer architecture. As can be seen from Fig. 3.16, we have set them to 120 and 250 for optimal speed.

### 3.3.5 Trotter splitting for higher order tensors

In order to derive the optimal decomposition of a higher order system tensor into multiple ER-tensors it is necessary to run a computationally demanding Star-MPS calculation first. Only this calculation yields a system tensor with its characteristic
entanglement structure. However, for a large number $N$ of environments this tensor becomes exponentially large $O(D^N)$ and its time-evolution infeasible.

We can overcome this issue by applying a Trotter decomposition to the effective Hamiltonian such that the time-evolution is performed separately for each environmental interaction

$$H_{eff} = \sum_{i} H_{eff}^i,$$

$$H_{eff}^i = \frac{H_S}{N} + H_{I,i} + H_{R,i},$$

where the system Hamiltonian is symmetrically split onto each environmental effective Hamiltonian $H_{eff}^i$. The speed-up is gained by performing a QR decomposition and time-evolving only the smaller matrix $R$ with the individual $H_{eff}^i$, while the isometry $Q$ is kept unchanged and contracted back after each Trotter step (Fig. 3.17). Benchmarks of a 5 environment model of DP-Mes show an up to 3 fold speed-up (Fig. 3.18). Although the accuracy of the method should increase with smaller $\Delta t$, we found a relative error of about $2-3\%$ against the simulation without Trotter decomposition across all time steps. Since this method is only used to get a quick approximation of the entanglement structure of $A$, this error can be considered negligible. For the application of this Trotter decomposition to simulations where accuracy is relevant, more thorough benchmarking would be advisable.

### 3.3.6 Benchmarks and Accuracy of ER-tensors

We assured sufficient convergence of simulations presented in Chapter 5 by sweeping the parameters limiting the maximum bond dimensions $D_{Node,max}$ and $D_{Chain,max}$ and comparing the results. As measure of accuracy we compare simulations with pairs $(D_{Node,max}, D_{Chain,max})$ to an expensive benchmark simulation by taking the relative mean absolute error $\varepsilon$ of the TT population kinetics. To find the performance optimum as balance between accuracy and computation time we present the error $\varepsilon$ against the CPU time needed to propagate the TTNS to the next timestep (see Fig. 3.19). We chose as benchmark $(120, 30)$ since results converged sufficiently and $t_{CPU}/\text{Sweep} = 10.2 \text{ min}$ was the upper limit to finish a simulation within 2 weeks. We found that the accuracy is mainly limited by $D_{Node,max}$ since any $D_{Chain,max} \in [20, 30]$ yielded very similar errors. With $\varepsilon < 3\%$, the optimal truncation bounds were set to $(80, 30)$ which gave a
3.3 Time-dependent variational principle

Fig. 3.18 Decreased CPU time when using Trotter splitting of $H^{\text{eff}}$ for the time-evolution of higher order tensors. Splitting the time-evolution of a 5 environment system tensor yields 2-3 times faster sweeps.

Fig. 3.19 Convergence in TTNS bond dimensions. Relative mean error $\varepsilon$ of $\hat{\rho}_{\text{TT}}$ with different maximum $(D_{\text{Node}}, D_{\text{Chain}})$ against $\rho_{\text{TT}}$ with $(120, 30)$, plotted against CPU time. The optimal trade-off is achieved for $(80, 20)$, where $\varepsilon < 3\%$ is sufficiently small.
total CPU time of 4 days on a single core of an Intel Xeon E5-2670 for the simulation of 1 ps.

To emphasise the tremendous amount of memory savings, here an example. At a fixed $D = 50$ the central tensor would have a size of $50^8 \times 16B = 564$ TB, while the ER-network has a size of only $6 \times 50^3 \times 16B = 11$ MB while maintaining most of the information.

3.3.7 Benchmarking multi-chain TDVP with the independent boson model

We will briefly demonstrate that our multi-chain TDVP implementation yields correct results by simulating the coherence decay of the independent spin boson model (iSBM) at $T = 0$. In Fig. 3.20 we present the coherence decay $|D(t)|$ of the 2-chain iSBM for Ohmic $s = 1$ (left) and super-Ohmic $s = 3$ (right) spectral functions with $\omega_{c,1} = 1$ and $\omega_{c,2} = 5$. The mean absolute errors are sufficiently low at a level of $10^{-4}$.

The exact result was obtained from the decoherence function by summing over the contributions of each chain

$$
\rho_{12}(t) = \rho_{12}(0)e^{-\Gamma_1(t)+\Gamma_2(t)} ,
$$

$$
\Gamma_i(t) = \int_0^{\omega_{c,i}} 2\alpha \left( \frac{\omega}{\omega_{c,i}} \right)^s \frac{1 - \cos \omega t}{\omega^2} d\omega .
$$

The mean absolute error for the Ohmic case is at $2 \times 10^{-4}$ and for $s = 3$ at $7 \times 10^{-4}$. The simulations were performed at a time step $\Delta t = 0.2$ and maximum dimensions $D = 30$, $d_{OBB} = 40$, and $d_k = 100$. 

3.4 Dynamic energy surfaces

One of the central operators relevant for the time-evolution of the TTNS and for finding the ground state in DMRG is the effective Hamiltonian of a site. This operator, constructed by contracting $\hat{H}$ with all tensors except for the tensor of the chosen site, contains all information relevant for the time-evolution of the site tensor. It is this remarkable property which allows us to gain deeper insights of the dynamics and its pathways. Here we will outline how we can derive the potential energy surface (PES) and the total energy surface (TES) from the effective Hamiltonian for the exciton system, as well as the corresponding adiabatic and non-adiabatic basis states.

3.4.1 Introduction: 2-level System

To introduce the concept we derive the energy surfaces of a simplified example (quantum double well). In a single mode spin-boson model (SBM)

$$\hat{H} = H_S + \lambda \sigma_z \frac{\hat{a}^\dagger + \hat{a}}{\sqrt{2}} + \omega_0 \hat{a}^\dagger \hat{a}, \quad (3.75)$$

with spin Hamiltonian $H_S = \frac{\Delta}{2} \sigma_x + \frac{\epsilon}{2} \sigma_z$, tunnelling rate $\Delta$, coupling $\lambda$, and mode frequency $\omega_0$, which is similar to the quantum Rabi model in case of vanishing energy level bias $\epsilon$, we can obtain the operator for the potential energy $\hat{V}$ by subtracting the kinetic energy $\hat{T} = \frac{\omega_0}{2}(\hat{p}^2 - \frac{1}{2})$

$$\hat{V} = H_S + \lambda \sigma_z \hat{Q} + \frac{\omega_0}{2} \left( \hat{Q}^2 - \frac{1}{2} \right), \quad (3.76)$$

where we used the mass-frequency normalised coordinates $\hat{Q} = \frac{\hat{a}^\dagger + \hat{a}}{\sqrt{2}} = \hat{x} \sqrt{\frac{m}{\omega}}$, $\hat{P} = i \frac{\hat{a}^\dagger - \hat{a}}{\sqrt{2}} = \hat{p} \sqrt{m \omega}$ and divided the zero point energy equally on $\hat{T}$ and $\hat{V}$. In the next step we replace bath operators by their scalar values $\hat{Q} \rightarrow Q$, $\hat{P} \rightarrow P$

$$H(Q, P) = H_S + \lambda \sigma_z Q + \frac{\omega_0}{2} \left( P^2 + Q^2 - 1 \right), \quad (3.77)$$

$$V(Q) = H_S + \lambda \sigma_z Q + \frac{\omega_0}{2} \left( Q^2 - \frac{1}{2} \right), \quad (3.78)$$

where the energies are now functions of the phase space coordinates $(Q, P)$. Plotting the eigenvalues of $V(Q)$ against $Q$ gives the adiabatic PES (dashed in Fig. 3.21). The corresponding eigenvectors map the diabatic spin states $|\uparrow\rangle, |\downarrow\rangle$ into the adiabatic basis.
Similarly, the eigenvalues of $H(Q, P)$ give the non-adiabatic TES and the eigenvectors form a non-adiabatic basis.

### 3.4.2 Multi-level Systems

In a similar fashion we can derive the energy surfaces for Hamiltonians with multiple states in the system and multiple environments. We will explain the necessary steps and implications at the example of DP-Mes. Furthermore we will give a more detailed investigation of the resulting energy surfaces and how they can be interpreted.

We can derive the potential $\hat{V}_{\text{star}}$ from $\hat{H}_{\text{star}}$ (Eq. (3.20)) for DP-Mes by subtracting the kinetic energy terms $\hat{T}_{i,k} = \frac{\epsilon_{i,k}}{2} \left( \hat{P}^2_{i,k} - \frac{1}{2} \right)$

\[
\hat{V}_{\text{star}} = H_S + \sum_{i=1}^7 \left( \overline{W}_i \| \lambda_i \| \hat{Q}_{i,0} + \hat{V}_{c,i} \right),
\]  
\[
\hat{V}_{c,i} = \sum_{k=0}^{N_i-1} \hat{V}_{i,k} + \sum_{k=0}^{N_i-2} t_{i,k} \left( a_{i,k}^\dagger a_{i,k+1} + h.c. \right),
\]  
\[
\hat{V}_{i,k} = \frac{\epsilon_{i,k}}{2} \left( \hat{Q}^2_{i,k} - \frac{1}{2} \right).
\]
At this point, it would not be useful to replace the bath operators by scalar phase space coordinates \((\hat{Q}_{i,k}, \hat{P}_{i,k}) \rightarrow (Q_{i,k}, P_{i,k})\) since this would yield a 2N-dimensional coordinate space which is impossible to analyse for \(N = 252\). Even the restriction to the RC only would still result in a 7D PES or 14D TES. Instead, we propose to only evaluate the operators along the trajectory taken by the time-evolved wave function

\[
|\Psi(t)\rangle = \sum_{l=1}^{d_s} \sum_{k=1}^{D} A^l_{1k}(t) |l\rangle |\phi_k(t)\rangle,
\]

which unravels the multi-dimensional energy surfaces into a single dimension, with time as the generalised reaction coordinate. Here, \(A^l_{1k}\) is the TTNS tensor for the electronic system and we know from the Schmidt decomposition that there are as many bath states \(|\phi_k(t)\rangle\) as there are system states \(|l\rangle\) for maximum system-bath entanglement. Each \(|\phi_k(t)\rangle\) can be interpreted as a particular bath configuration (displacement) or superposition of multiple bath configurations. We evaluate \(\hat{H}_{\text{star}}\) and \(\hat{V}_{\text{star}}\) by contracting them with the time-dependent bath-states

\[
H_{ik}^{\text{eff}}(t) = \langle \phi_i(t) | \hat{H}_{\text{star}} | \phi_k(t) \rangle,
\]

\[
V_{ik}^{\text{eff}}(t) = \langle \phi_i(t) | \hat{V}_{\text{star}} | \phi_k(t) \rangle,
\]

where \((H_{ik}^{\text{eff}})_{jl} = H_{ijkl}^{\text{eff}} = (H^{\text{eff}})_{(ij)(kl)}\) is the effective Hamiltonian of the system tensor \(A^l_{1k}\). To obtain surfaces similar to the ones described in the single-mode SBM, we would need to diagonalise \(H_{ii}^{\text{eff}}(t)\) and \(V_{ii}^{\text{eff}}(t)\), yielding the TES and PES created by \(|\phi_i(t)\rangle\) only. However, to understand the observed dynamics with strong system-environment entanglement, where the Born-Oppenheimer approximation breaks down, this picture is insufficient since there are also non-vanishing terms for \(j \neq l\) coupling different bath states. In order to account for them, we diagonalise the full effective operators \(H^{\text{eff}}(t), V^{\text{eff}}(t) \in \mathbb{C}^{D \cdot d_s \times D \cdot d_s}\)

\[
H^{\text{eff}}(t) = U_H(t) E_H(t) U_H^\dagger(t),
\]

\[
V^{\text{eff}}(t) = U_V(t) E_V(t) U_V^\dagger(t),
\]

yielding the non-adiabatic basis \(U_H(t)\) and corresponding TES in \(E_H(t)\), and the adiabatic basis \(U_V(t)\) with PES in \(E_V(t)\).
With access to the basis maps $U_H(t)$ and $U_V(t)$ we can also obtain the TES in the adiabatic basis and PES in the non-adiabatic basis as the diagonals of

\[
\tilde{E}_H(t) = U^\dagger_H(t) H_{eff}^H(t) U_V(t), \quad (3.87)
\]

\[
\tilde{E}_V(t) = U^\dagger_H(t) V_{eff}^V(t) U_H(t), \quad (3.88)
\]

which may also contain couplings since they are not purely diagonal any more.

**Associating electronic populations to the energy surfaces**

In addition to the PES and TES landscape we want to obtain information about the population of each surface in order to track the pathway of SF. Each system wave function associated with a bath state $j$ can be interpreted as an individual wave packet on the respective potential. By rotating the vectorised system tensor wave function $A \in \mathbb{C}^{D \times d_s}$ into the basis defining the PES/TES

\[
\tilde{A} = U^\dagger A, \quad (3.89)
\]

we can get the probability amplitude $\tilde{A}_k$ on each surface $k$. The population $\tilde{P}_k$ is then given by the element-wise product

\[
\tilde{P}_k = \tilde{A}_k \tilde{A}_k^* \quad (3.90)
\]

Furthermore we can calculate the contribution of each diabatic system state $i$ on each surface $k$ by using

\[
\tilde{P}_{i,k} = \sum_{j=1}^{D} U_{(ji),k}^* \tilde{P}_k \quad (3.91)
\]

Since this expression does not include coherences between surface (adiabatic) states, it yields incorrect diabatic populations when summing over $k$ and can only be taken as an estimate. Vice-versa, we can calculate the contribution of each surface $k$ to each diabatic population $P_i$ via

\[
P_{k,i} = \sum_{j=1}^{D} U_{(ji),k} \tilde{P}_i \quad (3.92)
\]

which will yield incorrect surface populations when summing over $i$ since the coherences between diabatic states are not included.
3.4 Dynamic energy surfaces

Fig. 3.22 Each of the two bath states $|\phi_k\rangle$ creates a set of energy surfaces, similar to the Born-Oppenheimer picture. When considering non-Born-Oppenheimer dynamics, the entanglement between the system and the bath demands simultaneous consideration of the individual surfaces, as shown in the lower panel. Any coupling terms between different $|l\rangle |\phi_k\rangle$ surfaces will cause shifts in energies and mixing between surfaces due to the diagonalisation procedure explained in the main text.

Energy surfaces in adiabatic and non-adiabatic basis

The TES in its non-adiabatic basis are displayed in Fig. 3.23. Since the effective Hamiltonian is diagonal in this basis, there is no residual coupling between the surfaces. Although the figure is difficult to interpret we can identify already a few key aspects. For each electronic state (coloured dots) we obtain 5 surfaces due to 5 different environmental states. This is especially evident from the fact that already for a single electronic state, its surfaces can take very different shapes which are caused by the different environmental configurations and movements. Also, surfaces of the same electronic state can span a wide range of energies which indicates that the associated potentials and environmental excitations are very different and can cause differences of up to 800 meV.

To give an example of how we can track the electronic population on top of the surfaces, we present in Fig. 3.24 the TES (a,c) and PES (b,d) plotted with respect to two different basis states and at a higher magnification. In particular, we distinguish between the non-adiabatic energy eigenstates $U_H$ of $H_{\text{eff}}$ (a,b), the adiabatic states $U_V$ (c,d), and the diabatic basis of the electronic system (colour of fills). The filled areas indicate by how much the surface is populated, while the colours give an estimate of diabatic mixing. This way of visualising the dynamics gives us a powerful tool to
Fig. 3.23 The TES of DP-Mes contain 5 surfaces per electronic state due to 5 different environmental states.

asses the underlying character of the dynamics. In this example we can identify an avoided crossing in the non-adiabatic TES as a key ingredient in the dynamics since it drives the LE\textsuperscript{+} to TT conversion. This avoided crossing is confirmed in comparison with the adiabatic TES which does contain coupling terms which are not captured by the basis and thus exhibits a crossing between TT and LE\textsuperscript{+}. The adiabatic PES in turn shows no significant crossing between the occupied TT and LE\textsuperscript{+} surfaces and thus excludes the possibility of a conical intersection in the observed dynamics.

The breakdown of the surface populations into the individual diabatic electronic state shows that the LE\textsuperscript{+} surface is fairly strongly mixed with the LE\textsuperscript{−} and the CT\textsuperscript{+} states. As we will show later, this is the main reason for the lowering of the LE\textsuperscript{+} TES below the TT TES. Subsequently the mixing reduces and the LE\textsuperscript{+} surface rises in energy.

**Partial diagonalisation**

To obtain a more profound understanding of the effective Hamiltonian and the reaction pathways it allows, it can be insightful to look at non-diagonalised forms because they expose the time-varying vibronic couplings within the model. Plotting the entire effective Hamiltonian over the simulated time range is not feasible which is why we
Fig. 3.24 Population of the TES (top) and PES (bottom) in the adiabatic (right) and non-adiabatic (left) basis within the first 200 fs. The surfaces (dots) are coloured according to the mixing of electronic states. Full population (fills) corresponds to 15% of the plot height. The amount of diabatic electronic population on each surface is highlighted with patches.
Fig. 3.25 (a) The unaltered diagonal of $H^{eff}$ exhibits simultaneous surface crossings within the same electronic state, which are artefacts due to inter-bath state coupling. (b) Partial diagonalisation of $H^{eff}$ with respect to a single electronic state only, and application of the found transformation to all other electronic states eliminates the artefacts. In this picture there is mostly only coupling between surfaces of different electronic character. Thus, the LE$^+$ surfaces are well above the TT TES in contrast to the fully diagonalised TES.

will focus on the diagonal elements as before, while keeping in mind that, depending on the applied transformation, there may be coupling terms between the resulting surfaces. A visualisation of the diagonal of the unchanged $H^{eff}$ (Fig. 3.25a) shows that there are a couple of sharp unphysical crossings between surfaces of the same electronic character. This indicates that there exists coupling between the environmental states which distorts the overall picture.

We can improve on this by only partially diagonalising $H^{eff}$. In particular, we look for a unitary $U_{H,j}(t)$ such that there are no couplings between states $|j⟩|φ_i⟩$ and $|j⟩|φ_k⟩$, meaning that

$$U_{H,j}^\dagger H_j^{eff}U_{H,j},$$

interpreted as a matrix product is diagonal, where $(H_j^{eff})_{ik} = H_{ijk}^{eff}$ is the corresponding block. In Fig. 3.25b we took the map $U_{H,2}(t)$ which diagonalises the LE$^+$ block and applied it to all other blocks. This nearly diagonalises all blocks $H_j^{eff}$ simultaneously, except for one entry in the TT block (see Fig. 3.26). The resulting plot is cleaner and does not show the additional surface crossings, while being yet very similar to the original $H^{eff}$. The discrepancy to the fully diagonalised $H^{eff}$ (Fig. 3.23) is
### 3.4 Dynamic energy surfaces

| \( |\phi_i\rangle\) | \( |\phi_j\rangle\) | \( |\phi_k\rangle\) | \( |\phi_l\rangle\) | \( |\phi_m\rangle\) | \( |\phi_n\rangle\) |
|---|---|---|---|---|---|
| 1.94 | 1.96 | 0.01 | 2.01 | 2.1 | 2.16 |
| 0.01 | 2.1 | 2.32 | 0.04 | 0.27 | 0.32 |

Fig. 3.26 The absolute values in eV of the effective Hamiltonian, partially diagonalised in the basis of the \( \text{LE}^+ \) sub-block, at \( t = 52 \) fs. The blocks correspond to electronic states, their diagonal elements are coloured according to the electronic state. For each electronic state there are five environmental states \( |\phi_i\rangle\). The off-diagonal elements are couplings between diabatic electronic states mediated by the environment. Their values reach up to 370 meV, large enough to lower \( \text{LE}^+ \) to cross the TT TES. Complete diagonalisation of this matrix yields the surfaces in Fig. 3.23.

Therefore caused by all remaining off-diagonal entries, which resemble couplings between different electronic states entirely mediated by the environmental states. The couplings reach values of up to 370 meV which agrees with the lowering and raising of the TES observed upon full diagonalisation. We can even assign the couplings to the action of specific environments. As an example, the coupling of 170 meV between \( |\text{LE}^+\rangle |\phi_1\rangle \) and \( |\text{LE}^-\rangle |\phi_2\rangle \) is due to the \( B_2 \) modes, while the 370 meV coupling between \( |\text{LE}^+\rangle |\phi_1\rangle \) and \( |\text{CT}^+\rangle |\phi_3\rangle \) is due to the \( B_1 \) modes.

This example shows that the typical approach of looking at the energy surfaces created by only a single environmental state, as employed in the Born-Oppenheimer picture, is not sufficient here. It is especially the couplings between states \( |j\rangle |\phi_i\rangle \) and \( |l\rangle |\phi_k\rangle \) for \( j \neq l \) and \( k \neq i \) which determine these strongly entangled, non Born-Oppenheimer, multi-state, and multi-environment dynamics. Unfortunately, this simultaneously increases the complexity of the associated energy surfaces, but we presented ways to alleviate this issue and gain further insight into the simulated
Hamiltonian. The transformations explained above at the example of the effective Hamiltonian can be equally applied to the effective potential.

### 3.5 Transfer Tensors

We implemented the transfer tensor technique as outlined by Cerrillo and Cao [25] in a similar fashion as described previously for TEDOPA [102] for its appealing possibility to learn the memory kernel of an arbitrary environment. We will briefly present the key features and describe how to extract the transfer tensor from a MPS calculation following Ref. [25].

The time-dependence of a reduced density matrix $\rho$ can be captured by dynamical maps $\mathcal{E}_k$ at discrete times $t_k$ as

$$\rho(t_k) = \mathcal{E}_k \rho(0), \quad (3.94)$$

where $\mathcal{E}_0 = 1$. With quantum process tomography [6], we can extract these dynamical maps which contain full information about the effect of the environment on $\rho$. For Markovian processes we could find $\mathcal{E}_k = \mathcal{E}_1^k$ which demonstrates the absence of memory and the sole dependence on the current state of $\rho$.

The set of $\mathcal{E}_k$ is very large and contains redundant information that can be captured more efficiently by means of transfer tensor defined as

$$T_{n,0} = \mathcal{E}_n - \sum_{m=1}^{n-1} T_{n,m} \mathcal{E}_m, \quad (3.95)$$

where the tensors $T_{n,m}$ capture the dependence of $\rho(t_n)$ on the state of $\rho(t_m)$. With these tensors we can obtain the time-dependence of $\rho$ as

$$\rho(t_n) = \sum_{k=0}^{n-1} T_{n,k} \rho(t_k). \quad (3.96)$$

If the initial system-bath conditions are separable and for a time-independent Hamiltonian, time-translation invariance can be used to reduce this equation to

$$\rho(t_n) = \sum_{k=0}^{n-1} T_{n-k} \rho(t_k), \quad (3.97)$$
where the transfer tensors are only encoding changes for relative time differences instead of fixed points in time. By comparing Eq. 3.97 with the Nakajima-Zwanzig equation in the Schrödinger picture

\[
\frac{\partial}{\partial t} \rho_S(t) = L_S \rho_S(t) + \int_0^t K(t, s) \rho_S(s) \, ds, \tag{3.98}
\]

we can relate the transfer tensors to the memory kernel \( K \) as

\[
T_{n-k} = (1 + L_S \delta t) \delta_{n-k,1} + K_{n-k} \delta t^2. \tag{3.99}
\]

The key insight is that for environments with a maximum memory time, the transfer tensors decay sufficiently over this timescale since the memory kernel vanishes and their series can be truncated. This allows a massive reduction in parameters and an extrapolation of dynamics as soon as a sufficient set of transfer tensors is found.

### 3.5.1 Ancilla-assisted quantum process tomography

We calculate the transfer tensors by performing an ancilla-assisted quantum process tomography as described by Altepeter et al. [6]. The ancilla is a site, identical to the system and neighbouring it, but fully uncoupled. This ancilla and the system will be prepared in a maximally entangled state \(|\Psi_{AS}\rangle\ |

\[
|\Psi_{AS}\rangle = \sum_{i=1}^{d_1} \frac{1}{\sqrt{d_1}} |n_{A,i}\rangle |n_{S,i}\rangle, \tag{3.100}
\]

that is easy to create as an MPS. In particular, the tensors for site 1 being the ancilla and site 2 being the system can be written as

\[
A(1)_{1,i} = \frac{1}{\sqrt{d_1}}, \tag{3.101}
\]

\[
A(2)_{i,1} = 1, \tag{3.102}
\]

with all other entries being zero, and \( d_1 \) the size of the system’s Hilbert space. The full initial state is then prepared as a product state between \(|\Psi_{AS}\rangle\) and the desired environmental state.

During the time-evolution of this initial state with TDVP, we extract the dynamical maps from the ancilla-system reduced density matrix \( \rho_{(im)(ij)} \), were \( l, m \) index the ancilla and \( i, j \) the system. We construct the simplest possible orthonormal operator
basis of the ancilla Hilbert space

\[ B_{(lm)k} = \delta_{(lm)k}, \quad (3.103) \]

where \( B \in \mathbb{C}^{d_1^2 \times d_1^2} \). In the next step we contract \( B \) with the ancilla part of \( \rho \)

\[ \mathcal{E}_{(ij)k} = d_1 \cdot B_{(lm)k} \rho_{(lm)(ij)}, \quad (3.104) \]

to find the full dynamical map \( \mathcal{E}_n \) for the current time step \( t_n \). Then the corresponding transfer tensor can be calculated as

\[ T_n = \mathcal{E}_n - \sum_{m=1}^{n-1} T_{n-m} \mathcal{E}_m. \quad (3.105) \]

### 3.5.2 Compression of transfer tensors

Since the transfer tensors \( T_i \in \mathbb{C}^{d_1^2 \times d_1^2} \) increase rapidly with increasing size of system Hilbert space, I developed a compression based on the low-rank tensor approximation to save memory and computational effort.

We can exploit the self-adjointness of the density matrix \( \rho_{ij} = \rho_{ji} \) to derive that the transfer tensors have to be self-adjoint as well.

\[ \rho'_{ij} = T_{ikjl} \rho_{kl} = \rho'_{ji} = T_{jikl} \rho_{kl}, \quad (3.106) \]

\[ T'_{ikjl} = T_{jikl}. \quad (3.107) \]

Thus, for \( (T)_{(ik)(jl)} = T_{ikjl} \) we find \( T = T^\dagger \). This condition means that we can use the eigendecomposition of \( T \)

\[ T = U \Lambda U^\dagger, \quad (3.108) \]

and only have to store the matrix \( M = U \sqrt{\Lambda} \). Since the eigenvalues exhibit an exponentially decaying spectrum, we can also apply truncation to achieve a low-rank approximation of \( T \).

### 3.5.3 Preliminary results for the Ohmic SBM

The transfer tensors were extracted both, for factorising initial conditions and for a polarised coupled state. We extracted transfer tensors for ohmic SBM calculations.
3.5 Transfer Tensors

Fig. 3.27 Norm of transfer tensors for an initial vacuum environment, learnt at $\Delta t = 0.02$. For $\alpha \geq 0.05$ the tensor norm did not decrease sufficiently.

Fig. 3.28 Norm of transfer tensors across learning time for a polarised coupled environment, learnt at $\Delta t = 0.1$. For $\alpha \geq 0.5$ the tensor norm did not decrease sufficiently (calculations terminated early).
under factorising initial conditions (Fig. 3.27) at time step $\Delta t = 0.02$ and under polarised coupled conditions (Fig. 3.28 and 3.29) at time step $\Delta t = 0.1$. Only for weak coupling $\alpha = 0.01$ the tensor norm dropped sufficiently below $10^{-4}$ to yield accurate results while for $\alpha \geq 0.5$ the results start deviating from the MPS simulations already soon after the learning period, as a result of the large residual norm indicating very long correlation times (Fig. 3.29). The TTM extrapolation for $\alpha = 0.5$ does not reach $\langle \sigma_z \rangle = 0$, while for $\alpha = 0.75$ $\langle \sigma_z \rangle$ decreases monotonically and even becomes negative.
Appendix 3.A  Lanczos Algorithm

The Lanczos algorithm [67] plays a central role in the orthogonal polynomials chain mapping of discrete environments and in the Krylov subspace algorithm used to perform the time evolution.

This algorithm is commonly used to bring hermitian matrices onto tridiagonal form. In order to do so, it creates an orthonormal basis $V$ which are a discrete version of the orthogonal polynomials discussed in Sec. 3.1.2. This basis also coincides with the basis of the Krylov subspace needed in the time-evolution.

The original Lanczos algorithm is unstable, leading to a rapid increase of non-tridiagonal entries. This instability is mainly due to a loss of orthogonality of $V$, which can be overcome by performing additional Gram-Schmidt orthogonalisation steps. For the construction of a large basis the Gram-Schmidt procedure becomes computationally expensive, since it orthogonalises the newly added vector against all previous vectors.

The algorithm can be improved by employing only a partial reorthogonalisation [111]. This scheme estimates the degree of orthogonality in each iteration and performs a full orthogonalisation step below a certain threshold. Additional gains can be achieved by employing a restarted Lanczos algorithm [36].

Appendix 3.B  Detection of numerical instability

An important task in any simulations which involve approximations, such as the bond truncation, is to proof the convergence of the results with respect to the parameters controlling the approximation. Detecting the convergence can be difficult in situations where it is not possible to spend any more resources due to insufficient computational power. For Figure 3.30 we demonstrate a case where the time step $\Delta t$ is chosen too large resulting in integration errors (see Fig. 4.4 for comparison). The error magnitude depends here on the coupling strength $\alpha$ and grows for larger $\alpha$. The numerical instability causing these errors exhibits architecture-dependent deviations which offers a way to asses the convergence of simulations without changing the related parameter $\Delta t$. 

Appendix 3.C  Imaginary time-evolution for thermal states

To study the influence of temperature on dynamics it is possible to perform an imaginary time-evolution to produce a thermal (environmental) state that can be used as a starting point for a subsequent real time-evolution. The thermal state is prepared from a state at infinite temperature $\beta = \frac{1}{k_B T} = 0$, by means of the thermal evolution.

Since a thermal environmental state is not pure, it needs a different representation than a standard MPS. A common solution is the conversion of the MPS into an MPO, such that each site is effectively represented by a density matrix [103, 130]. This has a major disadvantage for bosonic systems, where the local Hilbert space is large such that the MPO adds significant unfavourable computational effort in any kind of contraction. Another solution is the ancilla method, which purifies the thermal density matrix, allowing a representation as a pure MPS. Here, each bosonic site is prepared in a maximally entangled state with its ancilla before applying the thermal evolution [130].

Fortunately, the concept of OBB can be applied here to form a more optimal tensor network than reported before in literature. The tensor network in Fig. 3.31 consists of a standard MPS chain that has two layers of tensors fulfilling different purposes. During the thermal cooling down from $\beta = 0$, the bosons and their ancillas can occupy highly excited states at the order of $n = 10^2$ or more, depending on the simulated...
Fig. 3.31 Optimal tensor network for the implementation of ancilla-assisted thermal evolution. The OBB matrices allow dynamic reduction of local Hilbert space, as necessary during the evolution from infinite to finite temperature. The tensors combining bosons and ancillas are initialised to create maximally entangled states.
model, while at the final temperature (e.g. \( T = 300 \text{K} \)) \( n \) reduces by 1 or 2 orders of magnitude. Therefore, it is useful to introduce a layer of OBB matrices that allow a dynamic reduction from the local to the optimal Hilbert space. Since the maximally entangled state involves the full bosonic and ancilla Hilbert space, the OBB matrices are initialised as identity matrices. The OBB matrices of ancilla and boson are then connected to the MPS by means of a order 3 tensor \( M \), which can be interpreted as an ER-tensor as introduced in Sec. 3.2.6. This tensor combines ancilla states \( |a_k\rangle \) and boson states \( |b_k\rangle \) and simultaneously prepares the maximally entangled state \( |c_k = 1\rangle \) as
\[
M^{a_k,b_k}_{c_k} = \frac{1}{\sqrt{d_k}} \delta_{c_k,1} \delta_{a_k,b_k}.
\] (3.109)

The thermal evolution is then performed until \( e^{\beta H/2} \) in appropriate steps. Especially in the initial high temperature regime the entanglement and thus required bond dimension increases rapidly. Starting the tensors with too many excess dimensions leads to numerical instabilities which makes it necessary to employ a rapid yet precise bond expansion scheme. For minimal errors it is necessary to allow large \( D \approx 100 \) which slows down the thermal and subsequent time evolution.

A possibly more efficient method is the thermofield approach of de Vega and Bañuls [33]. The authors introduce ancilla sites and apply a thermal Bogoliubov transformation to transform an environment in a thermal state into 2 environments with different spectral densities but vacuum states, which together emulate the thermal environment. Since both thermofield environments are initialised in their vacuum states, the thermal evolution is avoided and the initial bond dimensions for the time evolution are drastically reduced. Furthermore, the Ansatz is analytic such that the thermal state is exact.
Chapter 4

Spin Boson Model Simulations

The initial phase of this work comprised the implementation of various state-of-the-art techniques which have been developed and reported before by other groups, but they have never been combined in a single software package. Since the aim of this work is to simulate the closed exciton-phonon quantum dynamics of large organic complexes, a task that is particularly difficult due to the large bosonic Hilbert spaces, it was imperative to produce this package to harness the individual strengths of the techniques simultaneously. The code base1 for variational matrix product states with optimised boson basis (OBB) and bosonic shift, developed by C. Guo [52], was the most advanced and available program for the simulation of ground states of the spin-boson model. Initial simulations testing the capabilities of this code are presented in Section 4.3. For the study of dynamical properties we further developed upon the time-dependent variational principle (TDVP), which was proposed by Haegeman et al. [54, 55], but only formulated the algorithm for the basic MPS. After adapting the TDVP to work with the OBB (see Sec. 3.3) and adding the orthogonal polynomials chain transformation (see Sec. 3.1.2), we tested both by simulating the dynamics of the SBM as presented in Section 4.4. The access to the environmental wave function allowed us to take a deeper look into the environmental dynamics and the effect on the two-level-system energy gap renormalisation.

This chapter has been published in F. A. Y. N. Schröder and A. W. Chin, Physical Review B 93, 075105 (2016). © 2016 by the American Physical Society. Collaborative work on the dynamics of the sub-Ohmic SBM, which is not presented here, led to the publication Gonzalez-Ballestero et al. [50].

1https://github.com/entron/bosonic-vmps
4.1 Introduction

Dissipative quantum dynamics can now be probed in microscopic, real-time detail, yielding unprecedented insight into system-environment processes whose understanding and control will be essential for future quantum technologies [30, 38, 42, 56, 101, 108]. Recently, experimental observations of coherence in organic and biological materials [10, 30, 38, 41, 49, 86, 101] have strongly motivated a better understanding of the microscopic origin and role of “ultrafast” (<ps) effects resulting from quantum correlations, memory, bath structure, and non-perturbative system-bath couplings. While advanced reduced density matrix techniques can account for these phenomena [58, 60, 63, 88], information is inevitably discarded when tracing out the environment, and a truly many-body approach is required for deeper insight into the mechanisms at play. However, this necessitates the evolution of a macroscopically large system-environment state, and the determination of open-system ground states and dynamics are only tractable with powerful computational techniques, such as exact diagonalisation, multi-configurational Hartree-Fock and various time-dependent (density matrix) renormalisation group techniques [7, 20, 53, 92, 96, 132].

In this chapter, we present a versatile new approach to this problem, based on the recently proposed time-dependent variational principle (TDVP) for variational matrix product states (VMPS) [43, 53, 55, 75, 103, 136]. This many-body method gathers together several recent advances in VMPS theory to create a fast, efficient algorithm for system-bath dynamics, where resources can be allocated “on the fly” [53, 55, 75]. We show that the method can correctly capture the complex, non-Markovian physics of the famous spin-boson model (SBM) [71, 137], and then show how visualizing the accompanying environmental dynamics provides an informative, time- and frequency-resolved spectroscopy of open systems. This combination of accurate system dynamics and powerful diagnostic tools for analysing the detail within system-environment states can be applied to a wide range of problems, and could be particularly useful for unravelling the physics of the “intermediate” regime of open systems [81].

The chapter is organized as follows. Section 4.2 defines the model Hamiltonian used in our calculations. Section 4.3 presents ground state calculations of the Ohmic SBM. Finally Section 4.4 presents dynamics of the Ohmic and sub-Ohmic SBM from weak to strong coupling and demonstrates to which detail the environmental dynamics can be analysed and related to system-bath dynamics.
4.2 The spin-boson model

The spin-boson model (SBM) has become the benchmark for testing advanced open system methods, as well as having numerous direct applications in physics, chemistry and biology [71, 137]. It describes a quantum two-level system (TLS) that interacts with an environment of harmonic oscillators via the Hamiltonian ($\hbar = 1$) [71],

$$H = -\frac{\Delta}{2} \sigma_x - \frac{\epsilon}{2} \sigma_z + \frac{\sigma_z}{2} \sum_n \lambda_n (b_n + b_n^\dagger) + \sum_n \omega_n b_n^\dagger b_n,$$

(4.1)

where the TLS has an energy bias $\epsilon$, coherent tunnelling amplitude $\Delta$, and coupling $\lambda_n$ to environmental modes of energy $\omega_n$. The operators $\sigma_i$ are Pauli matrices, while $b_n^\dagger$ and $b_n$ are bosonic creation and annihilation operators. Here, we focus on general power-law spectral functions $J(\omega) = \pi \sum_n \lambda_n^2 \delta (\omega - \omega_n) = 2\pi \alpha \omega_c^{1-s} \omega^s \theta (\omega_c - \omega)$ which parametrize the bandwidth of the environment $\omega_c$, the (dimensionless) interaction strength $\alpha$, and the frequency-dependence exponent $s$ which defines sub-Ohmic ($s < 1$), Ohmic ($s = 1$), and super-Ohmic ($s > 1$) environments. The Ohmic and sub-Ohmic cases possess a range of quantum phase transitions (QPT) ($\langle \sigma_z \rangle_{g.s} \neq 0$) when $\alpha$ exceeds a critical coupling $\alpha_c$ [7, 8, 12, 13, 19, 20, 27, 53, 63, 70, 88, 92, 128, 140, 146, 150].

4.3 Ground state properties

4.3.1 Logarithmic discretisation

To apply tensor network states, the SBM needs to be transformed into a semi-infinite chain, with the spin system at the first position. To study ground state, low energy and critical properties, the combination of logarithmic discretisation and mapping onto a Wilson chain with the Lanczos algorithm, as described below, has proven to be very successful and accurate since it can efficiently capture the low frequency spectrum of the spectral function [53].

The spectral density will be first discretised with the logarithmic scheme described in Ref. [21, 153]:

$$\omega_0^z = \omega_c,$$

$$\xi_i = \frac{\int_{\omega_i}^{\omega_{i+1}} J(\omega) \, d\omega}{\int_{\omega_i}^{\omega_{i+1}} \frac{J(\omega)}{\omega} \, d\omega},$$

$$\gamma_i = \sqrt{\int_{\omega_i}^{\omega_{i+1}} J(\omega) \, d\omega}. $$

(4.2)

(4.3)
Substituted in the Hamiltonian this gives

\[ H = H_{\text{spin}} + \sum_{n=0}^{\infty} \xi_n b_n^\dagger b_n + \frac{\sigma_z}{2} \sum_{n=0}^{\infty} \frac{\gamma_n}{\sqrt{n}} \left( b_n + b_n^\dagger \right). \] (4.4)

Following the NRG procedure, this star-like Hamiltonian can be transformed to the Wilson chain using a Lanczos tridiagonalisation scheme

\[ H = H_{\text{spin}} + \sigma_z \frac{\sqrt{\eta_0}}{\pi} \left( a_0 + a_0^\dagger \right) + \sum_{n=0}^{\infty} \left[ \epsilon_n a_n^\dagger a_n + t_n \left( a_n^\dagger a_{n+1} + a_{n+1}^\dagger a_n \right) \right], \] (4.5)

where \( \eta_0 = \int_0^{\omega_c} J(\omega) \, d\omega \) represents now the system-environment coupling due to \( J(\omega) \).

The site energies \( \epsilon_n \) decrease exponentially along the chain, thus choosing a finite chain length \( L \) defines a lower bound of the achievable precision of the model.

### 4.3.2 The Ohmic regime

In the region \( 0 < \alpha < 1 \) and \( \varepsilon \ll \Delta, \varepsilon \to 0 \) the longitudinal spin magnetization \( \langle \sigma_z \rangle \) undergoes a Kösterlitz-Thouless type quantum phase transition (QPT) between a delocalised phase where \( \langle \sigma_z \rangle \to 0 \) and \( \langle \sigma_z \rangle \to 1 \) for \( \alpha < \alpha_c \) and a localized phase where \( \langle \sigma_z \rangle \to -1 \) and \( \langle \sigma_z \rangle \to 0 \) for \( \alpha > \alpha_c \). A good description with derivations of this QPT can be found in Ref. [69].

The results produced by the VMPS agree very well with the Bethe Ansatz. In Fig. 4.1 the longitudinal magnetization \( \langle \sigma_z \rangle \) and transversal magnetization \( \langle \sigma_x \rangle \) as well as the entanglement entropy \( S \) are plotted against the coupling strength \( \alpha \) for different level asymmetries. As \( S \) and entanglement within the spin states rises towards the QPT, bond dimensions of the MPS rise because the entanglement between the system and the environment also increases, leading to more sweeps and longer calculation time. For reference, each point in the plot needed on average 25 sweeps equalling 2.5 minutes. The entanglement entropy \( S \) is identical to the earlier defined von Neumann entropy up to a factor \( S = S_{v\text{NE}}/\ln (2) \).

In the case of no level asymmetry \( \varepsilon = 0 \), the transversal magnetization goes as

\[ \langle \sigma_x \rangle_{\alpha > \frac{1}{2}, \varepsilon \to 0} = \frac{1}{2\alpha - 1} \frac{\Delta}{\omega_c}, \] (4.6)

from Ref. [69] which is shown in Fig. 4.2. At small \( \alpha \) above expression is not accurate enough resulting in the shown deviation, but at \( \alpha \to 1 \) the difference might be caused
4.3 Ground state properties

Fig. 4.1 Comparison of results for $\langle \sigma_z \rangle$, $\langle \sigma_x \rangle$ and the entanglement entropy $S$, obtained by Bethe Ansatz (top) from Ref. [69] and calculated with VMPS (bottom). The QPT in $\langle \sigma_z \rangle$ sharpens for vanishing level asymmetry $\varepsilon$.

by the VMPS. Since there is no level bias $\varepsilon$, small asymmetries in the code lead to an earlier localization of the spin close to the QPT at $\alpha_c = 1$. This can only be prevented by implementing parity symmetry explicitly.

4.3.3 The independent SBM

In the independent spin boson model (iSBM) where $\Delta = \varepsilon = 0$, the Wilson chain is highly occupied on the low energy sites at the end, similar to the localized regime $\alpha > \alpha_c$ in the sub-Ohmic SBM. To keep the operator and MPS dimensions low, an efficient and accurate bosonic shift has to be implemented (see Sec. 3.2.3). The advantage of the iSBM is that the displacement and occupation of the chain can be calculated directly from the Wilson chain parameters which I will briefly outline.
Spin Boson Model Simulations

Fig. 4.2 The transversal magnetization $\langle \sigma_x \rangle$ for $\varepsilon = 0$ and different values of $\Delta$ (a) and the relative deviation from the approximate analytical expression (b). The differences at $\alpha \approx 0.7$ are caused by the approximate nature of the analytical expression which results from approximations made in the mapping from the SBM to the Kondo model. At $\alpha = 1$ a deviation of 27% remains.

From the standard definitions for the translation, position, and momentum operators, the operator for a dimensionless displacement $f_n = x_n \sqrt{\frac{m \omega_n}{\hbar}}$ can be defined:

$$\hat{x}_n = (a_n^\dagger + a_n) \sqrt{\frac{\hbar}{2m \omega_n}}, \quad \hat{p}_n = i \left( a_n^\dagger - a_n \right) \sqrt{\frac{\hbar m \omega_n}{2}},$$

$$\hat{T}_n(x_n) = e^{-i \hat{p}_n x_n}, \quad \hat{T}_n(f_n) = e^{(a_n^\dagger - a_n)f_n}. \tag{4.7}$$

The ground state $|\Omega\rangle = U (f) |0\rangle = \prod_{n=0}^\infty \hat{T}_n(f_n) |0\rangle$ of the chain can be found by applying the unitary transformation $\hat{H} = U^\dagger H U$ to the Hamiltonian and finding $f_n$ such that all terms linear in $a_n$ and $b_n^\dagger$ vanish. The transformation effects:

$$a_n^\dagger \rightarrow a_n^\dagger + f_n, \tag{4.9}$$
$$a_n \rightarrow a_n + f_n, \tag{4.10}$$

and the displacements are found as the solution to:

$$\begin{pmatrix} \epsilon_0 & t_0 & 0 & \cdots \\ t_0 & \epsilon_1 & t_1 & 0 \\ 0 & t_1 & \epsilon_2 & \cdots \\ \vdots & 0 & \cdots & \cdots \end{pmatrix} \begin{pmatrix} f_0 \\ f_1 \\ f_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} -\frac{\sigma_x}{2} \sqrt{\frac{\hbar}{\pi}} \\ 0 \\ 0 \\ \vdots \end{pmatrix}. \tag{4.11}$$
Finally the relation to the bosonic shift defined in Eq. (3.36) is simply $f_n = \frac{\delta n}{\sqrt{2}}$.

The occupation $\langle n_k \rangle = \langle a_k a_k \rangle$ of the Wilson chain obtained with the VMPS is compared to the exact result in Fig. 4.3. The maximum relative deviation $<10^{-5}$ of the chain occupation confirms the high accuracy of the code. Nevertheless the shift procedure needed $\approx 130$ sweeps / 30 min, which is a ten-fold increase compared to the computations in Sec. 4.3.2, due to only a limited amount of possible shift per sweep. However if the regime of the calculation is known, a pre-estimated shift of the chain can minimize computation time.

### 4.4 Simulated SBM dynamics

The log-discretised and chain transformed SBM can also be used to study time-dependent, dynamical problems, but the discretisation introduces artefacts that are difficult to eliminate, due to insufficient sampling in the high-energy part of the spectrum. As a better approach for this type of studies we use the orthogonal polynomial mapping introduced in Chin et al. [26, 96] to obtain a semi-infinite 1D coupled-chain representation

$$
H = H_S + \frac{\sigma_z}{2} c_0 \left( a_0 + a_0^\dagger \right) \\
+ \sum_{k=0}^{L-2} \left[ \omega_k a_k^\dagger a_k + t_k \left( a_k^\dagger a_{k+1} + a_{k+1}^\dagger a_k \right) \right],
$$

(4.12)
with effective system-environment coupling \( c_0 = \sqrt{\int_0^{\infty} \frac{J(\omega)}{\pi} \, d\omega} \) and truncation of the chain to a length \( L \). This map is analytic for power-law \( J(\omega) \) and therefore does not need any discretisation (see Sec. 3.1.2). A subsequent artificial truncation of the semi-infinite chain introduces artefacts as soon as the wave function is influenced by the end-of-chain boundary effects, which is similar to truncating the Taylor series approximating the spectral function.

If not otherwise stated, we take \( \Delta = 0.1, \epsilon = 0, \omega_c = 1, \Delta t = 0.1 - 1 \) with initial MPS dimensions \( d_k = 30, D = 5, d_{OBB} = 5 \) and maximal \( D_{\text{max}} = 5, d_{OBB,\text{max}} = 15 \) in all simulations. All results had converged sufficiently with respect to \( D \) by \( D = 5 \). The required chain length \( L \) depends on \( \omega_c \), the simulated time range \( T \), and the extracted observables. If only the system dynamics are desired, we take \( L = \frac{2}{7} T \), while for environment observables in frequency space, we need \( L = \frac{2}{3.5} T \) to avoid artefacts caused by unphysical reflections at the end of the chain (see Fig. 4.8). For reference, a single sweep with dimensions \( d_k = 30, D = 5, d_{OBB} = 15 \), and \( L = 200 \) takes 4 seconds on one core of an Intel Core i7-4790 CPU.

We will consider two different initial state preparations for time evolution, both with the environment at zero temperature. The polarized coupled state is obtained via variational ground state optimization of the \( z \)-polarized spin coupled to the environment, as in Refs. [63, 92]. The uncorrelated product state has the vacuum state \( |\Omega\rangle \) of the bath coupled to the \( z \)-polarized spin.

### 4.4.1 Spin-dynamics

In Figs. 4.4-4.6 we present the dynamics in the weak \( (\alpha < \alpha_c) \) and strong coupling regime \( (\alpha > \alpha_c) \) for Ohmic \( s = 1 \) and sub-Ohmic \( s = 0.25, 0.5, 0.75 \) spectral densities. Globally, we find excellent agreement with previous numerical work on the non-Markovian dynamics of the SBM, such as the time-dependent numerical renormalisation group (TD-NRG) [92] and path integral methods [63]. In brief, the Ohmic results (Fig. 4.4) show increasingly damped oscillations as \( \alpha \) increases for \( \alpha < 0.5 \), overdamped relaxation for \( 0.5 < \alpha < 1 \) which relax more slowly as \( \alpha \rightarrow 1 \), and complete localization above the quantum-critical coupling of \( \alpha_c = 1 \).

The spin dynamics of the sub-Ohmic SBM close to the coherent-incoherent crossover \( \alpha_{CI}(s) \) are shown under the two different initial preparations of product state and coupled state in Figs. 4.5 and 4.6. In contrast to the Ohmic case, the sub-Ohmic dynamics always remain underdamped for \( s = 0.25 \), showing at least one oscillation even
Fig. 4.4 (a) Weak ($\alpha < \alpha_c$) and (b) strong coupling for Ohmic ($s = 1$, $\alpha_c = 1$) spectral density at different $\alpha$. Panel (b) was obtained at $\Delta t = 0.01$. 
Fig. 4.5 (a),(b) Weak and (c),(d) strong coupling (below and above $\alpha_c$) for sub-Ohmic spectral density ($s = 0.5, \alpha_c = 0.107$) at different couplings $\alpha$. Initial state is (a),(c) the product state and (b),(d) the coupled state.
Fig. 4.6 Weak and strong coupling (below and above $\alpha_c$) for sub-Ohmic spectral densities [(a),(b): $s = 0.25$, $\alpha_c = 0.022$; (c),(d): $s = 0.75$, $\alpha_c \approx 0.3$, $\alpha_{CI} \approx 0.22$] at different couplings $\alpha$. Initial state is the product [(a),(c)], or the coupled state [(b),(d)].
above $\alpha_c = 0.022$, as recently found in [63, 92, 146]. Furthermore an initial polarization of the bath leads to a higher frequency of spin oscillations with stronger coupling $\alpha$ which is not observable in the product state since the polarization persists on a larger time scale, giving an effective bias to the TLS Hamiltonian [88]. The frequency of these oscillations is non-monotonic, initially decreasing due to dressing of the tunnelling matrix element (a system-bath correlation effect) and then increasing for stronger coupling. The $s = 0.5$ case exhibits overdamping only with the product state for $\alpha > \alpha_{CI} \approx \alpha_c = 0.107$, while the coupled state always has initial oscillations even at strong coupling. The final value of $\langle \sigma_z \rangle$ reflects the mean field nature of the QPT in systems with $0 < s \leq 0.5$, for which the spin magnetization grows continuously from zero above the critical coupling [7, 27, 70, 140]. At $s = 0.75$ both the product state and the coupled state lead to overdamped dynamics for $\alpha \gtrsim \alpha_{CI} \approx 0.22$ and localize for $\alpha > \alpha_c \approx 0.3$. The accuracy of the calculations across a wide range of spectral densities from weak to strong coupling combined with the efficient use of computational resources demonstrates the versatility of the VMPS implementation.

### 4.4.2 Environment dynamics and spectroscopy

Having verified our method, we now use an efficient inversion of the chain mapping (see Sec. 3.1.2) to present the dynamics of the entire environment in time-frequency space\(^2\). Figure 4.7(a) and its inset show the population of each mode for intermediate Ohmic coupling, with an initially broad excitation and subsequent emergence of a sharp resonance peak around the TLS energy gap. The peak in this environmental “absorption spectrum” rises on the time scale of spin relaxation ($\omega_c t \approx 300$), while its position evolves and is complete by $\omega_c t \approx 110$. The final peak position is reached after about one period of the resonant frequencies of the environment modes ($\omega_{\text{res}} \approx 0.06\omega_c$), consistent with the “sampling” required for the broadband environment to resolve the TLS gap. A range of novel phenomena related to non-detailed balance and phase-dependent relaxation have recently been predicted to exist prior to this time [94], though we will not explore this further here.

Indeed, we note that this time scale may be additionally modified by polaronic dressing (spin-bath entanglement), which leads to a renormalisation (suppression) of

\(^2\)The dynamics in the chain basis $a_k$ are useful for monitoring the quality of the simulation, i.e. checking for reflections due to the finite length of the environment, and also aid the dynamic reallocation of resources by looking at the entanglement entropy and use of isometries along the chain. However, as the chain is an artificial expedient for performing the simulations, the original basis $b_n$ gives insight that is easier to relate to analytical theories.
Fig. 4.7 (a) Phonon modes $\omega_k$ occupation for an Ohmic environment with $\alpha = 0.2$ exhibits a strong resonance at the renormalized tunnelling amplitude $\Delta_r \approx 0.057$ and a damping of oscillations. (b) Simulated renormalized tunnelling $\Delta_r$ versus analytic expression (lines) shows good agreement. Polaron theory predicts $\Delta_r = \Delta e^{-\alpha s}$ for $s = 3$. (c) The projected phonon displacement $f_k^s$ for $s = 1, \alpha = 0.4$ oscillates even after spin relaxation at $t \approx 350$. 
the bare TLS energy gap $\Delta$ that drives Ohmic and sub-Ohmic ground states towards their QPTs. The environment spectrum in Fig. 4.7(a) clearly resolves the emergence of the renormalized TLS’s energy gap $\Delta_r$. This ultrafast process, dominated by high frequency ($\omega_k > \Delta$) modes, is generally hard to observe but important in organic exciton transfer and has been seen in inorganic semiconductors [56]. According to Silbey and Harris’ variational polaron theory for the ground state of the Ohmic SBM [110], $\Delta_r = \Delta \left( \frac{\Delta}{\omega_c} \right)^{\alpha_1 - \alpha_2}$, which agrees with the peak position extracted from the environmental spectra. This is shown in Fig. 4.7(b) for $s = 1$ and $s = 3$ in the regime $0 < \alpha \leq 1$.

In the chain basis the renormalisation is accompanied by the persistent excitation of the sites closest to the system, which defines an effectively screened system “seen” by the rest of the environment (see Fig. 4.8) – an observation familiar in NRG studies of the related Kondo problem [22]. The dynamics of the collective coordinate of the first chain site were also used to verify a novel coherence pumping mechanism in a recent study of a simple photosynthetic pigment-protein complex [29].

Accompanying the emission of phonons into the resonant modes, we also observe prominent, damped oscillations for all modes, which vanish on the time scale of spin relaxation (Fig. 4.7). Recently, Bera et al. have shown that strong coupling induces intermode entanglement which could induce apparent mixing and damping of individual modes [12, 13], but this is predicted for slow and resonant modes, whereas we find damped oscillations at all frequencies. Given the unitary, energy-preserving evolution of the many-body state, this observation warrants further consideration. To investigate this, we perform a type of state-selective coherent spectroscopy to look at further details within the many-body state. Figure 4.7(c) shows the displacement $f_k$ of modes projected onto the up spin state; i.e., we compute $f_k^{\uparrow} = \langle 1 \pm \sigma_z 2 b_k^\dagger b_k \rangle$. It is immediately seen that the displacements do not show any damping and oscillate at their natural frequencies over the length of the simulation.

Figure 4.9 shows the typical dynamics of a high-frequency mode. The positive and negative displacements for $|\uparrow\rangle$ and $|\downarrow\rangle$ are characteristic of polaronic entanglement between the spin and oscillator. However, it can be seen that their motion is highly correlated; maximum mode displacement on one spin state is always obtained at the minimum of the other. Moreover, the momentum of the mode in each spin state is the same and preserved; it is not randomized by the dissipative spin-flip dynamics. This classical correlation within the entangled state is important, and explains both the appearance of a stationary renormalized $\Delta_r$ and the apparent relaxation of the mode populations $\langle b_k^\dagger b_k \rangle$. To motivate this, consider the trial
Fig. 4.8 The occupation of the chain for $s = 1, \alpha = 0.2$ shows a clear constant offset on the first few sites indicating the dressing and renormalisation of the spin. Additionally the chain exhibits reflections from the end at $\omega_c t \approx 380$ leading to artefacts in the inverse chain mapping. The open system dynamics are correct until the arrival of the reflected waves at $\omega_c t \approx 760$. 
Fig. 4.9 (a) The occupation $\langle n_k \rangle$ and (b) the spin-projected displacements $f_k^\uparrow$ and $f_k^\downarrow$ of the mode $\omega_k = 0.325$ with initial product state.

Fig. 4.10 The phonon occupation for $s = 0.75, \alpha = 0.4$ with initial product state oscillates even after the relaxation of the spin oscillations at $\omega_c t \approx 150$ due to the finite $\langle \sigma_z \rangle \neq 0$. 
wave function $|\Psi(t)\rangle = C_\uparrow(t)|\uparrow\rangle|f^\uparrow_k(t)\rangle + C_\downarrow(t)|\downarrow\rangle|f^\downarrow_k(t)\rangle$, where we neglect the other environmental modes. The oscillator wave functions for each spin state are time-dependent coherent states $|f^\uparrow_k(t)\rangle = e^{i(f^\uparrow_k(t)b_k^\dagger - f^\uparrow_k(t)b_k)}|0\rangle$. The expectation value $\langle \sigma_x \rangle$ is then $\langle \sigma_x \rangle = 2\Re[C_\uparrow(t)C_\downarrow^*(t)\langle f^\downarrow_k(t)|f^\uparrow_k(t)\rangle]$. The oscillatory displacements we find fit $2f^\uparrow_k(t) \approx -\lambda_k\omega^{-1}_k(1 - e^{i\omega_k t})$ and $2f^\downarrow_k(t) \approx \lambda_k\omega^{-1}_k(1 + e^{i\omega_k t})$, after about one oscillation period. As $\langle \sigma_x \rangle$ is determined by the overlap of the oscillator wave functions entangled with each spin state, we see that the relative displacement of these wave functions is preserved for all further times, obeying $f^\downarrow_k - f^\uparrow_k = \lambda_k\omega^{-1}_k$. Thus the correlated motion provides a constant renormalisation of the spin tunnelling, which when summed over all modes leads to the $\Delta_r$ predicted by ground state theories and observed here as the peak position of the environmental absorption. Indeed, had the relative displacement been time-dependent then $\langle \sigma_x \rangle$ would not relax to a stationary value. Next we see that the mode population $\langle b_k^\dagger b_k \rangle = |C_\uparrow(t)|^2|f^\uparrow_k(t)|^2 + |C_\downarrow(t)|^2|f^\downarrow_k(t)|^2 = \frac{1}{2}(1 + \langle \sigma_z \rangle \cos(\omega_k t))$, again, we see the correlated motion only leads to oscillations of the population when the spin is out of equilibrium ($\langle \sigma_z \rangle \neq 0$), and explains why the apparent population damping for all high-frequency modes is set by the relaxation of the spin. Interestingly, this analysis predicts persistent population oscillations for $\alpha > \alpha_c$ in sub-Ohmic baths, or a biased TLS, which is confirmed in Fig. 4.10. However, we note that in real systems the environment must be connected, albeit weakly, to an external bath, and oscillations will vanish at very long times (all observables become stationary).

### 4.5 Conclusions

These results show how broadband environmental dynamics can be analysed at their various significant frequency scales. Indeed, we have only considered a small subset of the SBM physics; similar analysis must also be applied to resonant and slow frequency modes, the dynamical hierarchy and feedback between their contributions, and the role of any isolated modes, to build the full picture. This dynamical dissection, made possible by our VMPS many-body approach, not only offers new insights into the fundamental aspects of complex open systems; it may also guide the construction of cheaper Ansätze for describing their ground states and dynamics [12, 13, 58, 146, 150]. More immediately, the observation of conserved vibrational coherences during heavily damped spin relaxation has relevance for time-resolved observation of transfer, and activation and deactivation of vibrational coherences, recently shown to be a powerful tool for exploring ultrafast, coherent processes in optoelectronic systems and biological
photoreactions [10, 72, 73, 86]. Finally, we note that further extensions are required for general applications, many of which – such as finite temperatures and damping of the primary environment – have already been developed in related methods, such as the DMRG-based TEDOPA of Prior et al. [96].

**Appendix 4.A  Convergence of simulations**

To check the convergence of the presented simulations, we performed a series of simulations with bond dimensions $d_{OBB} = 40$, $D = \{5, 20, 150\}$ and with two time steps $\Delta t = 0.1$ (dots) and $\Delta t = 1$ (crosses) of the Ohmic SBM from weak to strong coupling $0 < \alpha = 1$. As a measure of accuracy we calculated the mean absolute relative error of the spin polarisation

$$
\varepsilon = \text{mean} |1 - \langle \sigma_z \rangle / \langle \sigma_z \rangle_{\text{best}}|,
$$

with respect to the most accurate simulation $\langle \sigma_z \rangle_{\text{best}}$ for $D = 150$ and $\Delta t = 0.1$ which had CPU times as given in Table 4.1. While for $\Delta t = 1$ and $D = 5$ the worst error is 13%, the errors of $D = 20$ and $D = 150$ are almost identical with a maximum of
Table 4.1 CPU times per sweep for the simulation $\langle \sigma_z \rangle_{best}$ with $D = 150$ and $\Delta t = 0.1$.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>0.01</th>
<th>0.05</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
<th>0.5</th>
<th>0.75</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{CPU}$/Sweep/min</td>
<td>0.96</td>
<td>1.27</td>
<td>1.32</td>
<td>1.51</td>
<td>1.73</td>
<td>3.00</td>
<td>4.14</td>
<td>3.40</td>
</tr>
</tbody>
</table>

3%. Decreasing the time step to $\Delta t = 0.1$ reduces the error of $D = 5$ to 2%. A larger $D = 20$ reduces the error by an order of magnitude but also doubles the computation time. The calculation with $D = 150$ takes additionally up to 4 times longer. Based on this evaluation we chose $\Delta t = 0.1$ and $D = 5$ for $\alpha < 0.5$. 

4.A Convergence of simulations
Chapter 5

Simulations of Singlet Fission in DP-Mes

Having verified and demonstrated the capabilities and computational efficiency of our MPS implementation and time evolution for bosonic environments, we turned towards the challenge of applying MPS to realistic exciton-phonon models of larger molecules. Due to the high complexity of natural light-harvesting complexes, we aimed for a more tractable dimer molecule, DP-Mes, which has been investigated experimentally in our group to assess its singlet fission characteristics. Its cruciform geometry leads to a decoupling of all electronic states, such that purely vibronic dynamics can be observed, which made it a good candidate for our method. A linear vibronic coupling (LVC) Hamiltonian was provided by D. H. P. Turban based on DFT/TD-DFT calculations. I developed the tree tensor network states and clustering techniques described in Chapter 3 to extend the capabilities of the original MPS and interface it with the LVC Hamiltonian. This chapter demonstrates that it is possible to objectively and reliably simulate vibronic dynamics of molecules with TTNS, in contrast to previous approaches which relied on approximations and a careful selection of only few vibrational modes, to limit the computational effort. Besides a more in-depth analysis of the correlation between system and environmental dynamics, I developed a novel method to calculate and visualise the energy surfaces upon which the vibronic non-Born-Oppenheimer dynamics are proceeding, as described in Section 3.4.

5.1 Introduction

Ultrafast open quantum dynamics have recently attracted considerable attention in the context of molecular light harvesting materials, where experimental evidence has begun to highlight the role of coherent, non-equilibrium vibronic dynamics in systems ranging from organic photovoltaics to the pigment-protein complexes of photosynthesis. Exploiting novel phenomena emerging from a complex interplay of vibrational, electronic and structural dynamics in tailored materials offers an exciting route towards advanced, next-generation light harvesting devices. The process known as singlet fission, which can occur in a wide variety of molecules and material phases, has recently emerged as a very promising arena in which to explore this.

In organic semiconductors such as pentacene, a photogenerated singlet exciton can undergo singlet fission (SF) into a pair of singlet-entangled triplet excitons on sub-100 fs timescales, efficiently generating two electronic excitations from a single incoming photon [14, 113]. Harnessing this potential carrier multiplication could help to overcome the Shockley-Queisser limit in photovoltaics [107]. Hence, understanding the links between the dynamics and efficiency of SF in a wide range of thin film, single crystal and solution-phase materials is attracting increasing interdisciplinary attention [4, 118, 129, 139, 148, 151]. Recently, ultrafast optical spectroscopy experiments have revealed how non-equilibrium and non-perturbative open quantum dynamics contribute to the ultrafast kinetics of SF, highlighting the role of intramolecular vibrations, conical intersections and vibronic mixing of triplet pair and bright excitonic states as drivers of ultrafast SF [10, 45, 80, 86, 114]. Importantly, these results indicate that the evolving quantum state of the molecular environment is highly correlated with the fate of photoexcitations and cannot be treated as a passive ‘heat bath’, as assumed in Markovian master equation studies of SF [15, 84].

As a result, we developed a tree tensor network state (TTNS), many-body wave function-based technique that exploits recent advances in matrix product states (MPS) [55, 104], machine learning, and entanglement renormalisation methods [127] to simulate open dynamics arising from multiple strongly coupling and highly structured vibrational environments.

Although our TTNS shares structural similarities with the Hartree-Fock method ML-MCTDH [132], its origins in condensed matter physics provide valuable improvements. Our method interfaces directly with ab initio electronic structure to obtain
model parameters and offers a very promising route to understanding, designing and discovering materials that exploit novel non-equilibrium dynamics.

As a suitable case study, we apply TTNS to an \textit{ab initio} DFT calculated model of a pentacene-based dimer molecule, 13,13'-bis(mesityl)-6,6'-dipentacenyl (DP-Mes, Fig. 5.1b), in which direct SF is symmetry forbidden \cite{76,77}, and demonstrate that the recently observed ultrafast (sub-ps) SF in this molecule arises from a rapid \textit{sequence} of symmetry breaking molecular motions that drive SF via vibronic super-exchange, emphasising the need for TTNS. Analysing the electronic dynamics, coherences, and environmental observables of the full many-body wave function, we pinpoint how ultrafast reorganisation of the different vibrational environments spontaneously create the couplings that ultimately generate $\approx 90\%$ TT yield. Going further, we then introduce a method to visualise these non-equilibrium dynamics as motions on environmental energy surfaces, obtained ‘on the fly’ from effective Hamiltonians generated by our TTNS wave function, which are otherwise inaccessible in reduced density matrix based methods. Crucially, we find that tensor network representations of open systems provide a completely general and intuitive way to discover the most relevant energy surfaces within the ultra high-dimensional configuration spaces of environments, enabling a clear identification of the physics underlying dissipative quantum processes which could be applied to a wide range of models and systems beyond SF. Here, we use this new capability to show that SF occurs in DP-Mes via an avoided crossing (AC), rather than a conical intersection (CI).

### 5.2 Electronic structure and vibronic model

\textit{Ab initio} TD-DFT calculations have been performed on DP-Mes to derive a microscopic Hamiltonian model, spanned by five electronic diabatic states, denoted system, directly relevant to SF at the computed cruciform geometry of the ground state (see Fig. 5.1). These states are the (anti)symmetrised local exciton states $LE^\pm$, the (anti)symmetrised charge-transfer states $CT^\pm$ and the final triplet pair TT. The $LE^+$ and $CT^\pm$ states are coherently delocalised over the two monomer units, leading to an optically bright $LE^+$ and dark $LE^-$ state (J-dimer). We find excited state energies of $2.07 \text{ eV (}LE^+\text{),}$ $2.20 \text{ eV (}LE^-\text{),} 2.75 \text{ eV (}CT^\pm\text{) and 1.83 eV (TT),}$ which define the diagonal of the system Hamiltonian $H_S$. Unlike the case of neighbouring pentacenes in thin films and molecular crystals, the molecular symmetry of the ground state geometry suppresses all electronic coupling between excited states, leaving $H_S$ strictly diagonal. Thus, although
Fig. 5.1 **Reaction pathways and modelling.** (a) Electronic states and their coupling through vibrational modes in DP-Mes (b), coloured by their symmetry within the point group $D_{2d}$. After photoexcitation of $\text{LE}^+$, SF can proceed via pathway I (dotted) or II (lines). (c) Once clustering identified symmetries and coupling patterns within the full vibrational environment (E), each cluster of modes is transformed onto chains to yield the model Hamiltonian. In the TTNS (right), all environmental states are connected to the electronic states (S) through a network of entanglement renormalisation (ER) tensors to improve speed and accuracy.
SF is strongly exergonic in this dimer it is strictly forbidden unless this symmetry is broken by vibrational motion (see Fig. 5.1), making this an ideal system for studying the role of vibronic quantum dynamics in SF. However, even with symmetry breaking, the effective coupling between LE and TT states, as in many ultrafast SF systems, is indirectly mediated by the high-lying CT states, leading to an effective super-exchange coupling of LE$^+$ and TT [14, 15, 113]. The coupling and energies of the CT states are therefore extremely important in SF materials, and must be included in the \textit{ab initio} and dynamical simulations, even if they are never populated [14].

We then employ further DFT calculations to construct a linear vibronic Hamiltonian

$$
\hat{H}_{LVC} = H_S + \sum_{n=1}^{318} W_n \frac{\hat{b}_n^\dagger + \hat{b}_n}{\sqrt{2}} + \hat{H}_{\text{vib}},
$$

based on the 318 quantum harmonic normal modes $\hat{b}_n^\dagger$ of the dimer’s ground state potential [66]. This describes the emerging electronic couplings $W_n$ as the system is perturbed from the ground state geometry. Modes below 110 cm$^{-1}$ and above 1500 cm$^{-1}$ were disregarded due to either unrealistic parameters arising from the neglect of their anharmonicities or irrelevance for present time-resolved experiments, respectively. Further details and limitations of the method are described in the Appendix 5.A.1. We note that, in contrast to phenomenological Holstein-like models, the $W_n$ can have diagonal and off-diagonal components, the latter being essential for SF in DP-Mes.

### 5.3 Interface to TTNS

Following previous t-DMRG and Matrix Product State (MPS) approaches, we transform $\hat{H}_{\text{vib}}$ into a system of independent 1D-chain environments (Fig. 5.1c) to reduce its complexity and allow simulations with tensor wave functions. The orthogonal polynomial chain transformation [26, 96, 104] exposes the low entanglement property of the environment. It can only be applied to modes with identical coupling pattern $W_n$ and arbitrary strengths $\lambda_n$, where $W_n = \lambda_n W_n$. However, our \textit{ab initio} patterns $W_n$ exhibit a variety that grows with the irregularity and size of the molecular structure. In order to group modes with similar $W_n$, we employ unsupervised machine learning in the form of k-means clustering (see Sec. 3.1.1). Thereby, we can find the minimal required set of environments $i$ and their coupling operators $W_i$ that optimally approximate $W_n$ of assigned modes. We find that DP-Mes couplings require a minimum of four clusters, as confirmed by group theory, one for each 1D irreducible representation (irreps) $A_{1/2}$.
and $B_{1/2}$ of the approximate point group $D_{2d}$ of DP-Mes. However, the large variances
of the couplings are only sufficiently described by seven clusters (see Fig. 3.1).

The transformation of each cluster into chains $\hat{H}_{c,i}$ yields the star-like Hamiltonian
(see Fig. 5.1c)

$$\hat{H}_{\text{star}} = \hat{H}_S + \sum_{i=1}^{7} \mathbf{W}_i \|\lambda_i\| \left(\hat{a}_{i,0}^\dagger + \hat{a}_{i,0}\right) \sqrt{2} + \hat{H}_{c,i},$$

(5.2)

where $\lambda_i = (\lambda_{i1}, \ldots, \lambda_{in})$, and $a_{i,0}^\dagger$ is termed the reaction coordinate (RC) of chain $i$,
which directly reflects collective motion and time scales of the bath. The matrices $\mathbf{W}_i$
and parameters of our 252 mode model are given in the Appendix 5.B.

### 5.4 TTNS for vibronic quantum dynamics

The model is simulated with tree tensor network states (TTNS), a low-rank tensor
approximation to the full vibronic system-environment wave function. Our approach
naturally extends the matrix-product state (MPS) method for open quantum systems
[53, 93, 96, 103, 104, 126, 131] to treat models with multiple bosonic environments.
We briefly outline the key features of our TTNS, while for technical details on MPS we
refer to Sec. 3.2.5 and the excellent reviews given in Refs. [93, 103].

Diagrammatically, the tensors (arrays) of a TTNS are represented as shapes with
one open bond (line) per array dimension. The multiplication of two tensors is drawn
as a joining of the respective bonds (see Fig. 5.2). Thus, a key figure regarding memory
requirements is the bond dimension $D$, the size of the array dimensions and equal to
the number of auxiliary states. $D$ governs the amount of entanglement that can be
simulated, as measured by the von Neumann entropy $S = -\text{Tr}(\rho \ln \rho)$, and typically
ranges within $D = 10 \text{–} 100$ for acceptable results. In a $N$-environment TTNS, the
central system tensor connecting to each bath suffers a curse of dimensionality, as its
size scales exponentially $\mathcal{O}(5D^N)$ in the number of its nearest-neighbours. Although
clustering and chain transformations reduced $N$ from 252 in $\hat{H}_{LVC}$ down to 7 in
$\hat{H}_{\text{star}}$, the central tensor requires 57 TB of memory. We compress the tensor down
to 40 MB by decomposing it into a tree network of smaller auxiliary entanglement
renormalisation (ER) tensors [39, 127] (Fig. 5.2). Their connectivity optimally exploits
inter-environment entanglement (blue) to minimise the entropy $S$ on all bonds, which
maximises the achievable accuracy at fixed $D$. This ER-tree reduces complexity to
$\mathcal{O}(ND^3)$ and is a key enabler for applying TTNS to $N > 3$ environment models.
5.5 Simulation Results

5.5.1 Fission dynamics in DP-Mes

Figure 5.3 presents electronic population dynamics (a) and the environmental occupation of the RCs across different orders of magnitude (b,c). Vibrationally mediated SF happens on a timescale of 200 fs (Fig. 5.3c), with a final TT yield of \( \approx 90\% \), comparable to experiments where yields around 94 % and timescales of 400 – 700 fs have been reported [76]. Considering the typical instrument response of 100 fs and the limitations of TD-DFT in vacuum, while experiments were performed in solutions, our results...
Fig. 5.3 Simulated SF dynamics in DP-Mes. Electronic populations (a) and environmental RC occupation dynamics (b,c). For < 20 fs damped Rabi oscillations transfer population from LE⁺ to LE⁻ and CT⁺. At subsequent times TT mirrors the LE⁺ decay leading to SF on a timescale of 200 fs and suggesting a direct SF pathway. Similar timescales are present in the bath excitation ⟨nRC⟩ of B₁ and B₂. The final TT yield reaches 90% after 1 ps.

are reasonably realistic. The dynamics are multiscale; at early times < 20 fs they are dominated by ultrafast damped vacuum Rabi oscillations (LE⁺ ↔ CT⁺, LE⁺ ↔ LE⁻, see Fig. 5.3a), with significant population transfer between LE⁺ and LE⁻ accompanied by rapid oscillatory excitation of the RCs of the B₂ environments coupling these states (see Fig. 5.9). The Rabi oscillations of CT⁺ correlate with the initial increase of TT population dρTT/dt indicating a small contribution of path I through A₂ (Fig. 5.4). This oscillatory exchange of quanta results from nuclear motion establishing mixed states between LE± and CT±, which is believed to be essential to SF [10, 11]. Following this mixing (> 50 fs), the population of the TT state quickly begins to rise, mirroring the decay of the LE⁺ state, and accompanied by strong excitation of the B₁ RCs. These vibrations couple both LE⁻ and TT via CT⁻, and thus open the vibronic super-exchange channel, labelled path II in Fig. 5.1. The appearance of a strong imaginary coherence Im(ρTT,LE⁻) indicates coherent transport between respective states. Since it matches the major increase in TT population dρTT/dt, it is a strong evidence that the B₁ super-exchange drives SF (see Fig. 5.4). Additionally the TT population is modulated by the fast A₁,₂ tuning modes which can be observed in vibrational spectroscopy. Although the model does not explicitly include dissipation, the vibrational
5.5 Simulation Results

![Graph showing simulation results](image)

**Fig. 5.4 Evidence for coherent transport.** The change $d\rho_{TT}/dt$ of $\rho_{TT}$ correlates with the dynamic coherence $\text{Im}(\rho_{TT,LE})$ indicating coherent super-exchange via $B_1$. The large oscillations with period of 20 fs correlate with $A_{12}$ oscillations (see Fig. 5.3b). The maximum SF rate is achieved at 90 fs during the passage of the avoided crossing in the TES.

Motion is slightly damped. This dissipation originates from anharmonicity induced by the tuning modes coupled to the electronic states, leading to energy transfer between coupling modes. It is remarkable that this purely harmonic mode model does achieve anharmonicity through the interaction of multiple independent environments.

The 5% CT$^-$ content shows that we reach a bound TT state which is lower in energy than a T+T (or non-relaxed TT state) [64, 114, 147]. The non-vanishing LE± on the other hand indicates that the equilibrium state can exhibit singlet character in its excited state absorption [76].

**5.5.2 Dynamic energy surfaces**

In the following, we calculate adiabatic potential energy surfaces (PES) and total energy surfaces (TES), which also include nuclear kinetic energy to investigate non-adiabatic dynamics, to gain a deeper understanding of the mechanism behind SF in DP-Mes. A major difficulty of visualising energy surfaces for $N > 2$ vibrational modes is that the coordinate $\mathbf{x} = (x_1(t), \ldots, x_N(t))$ is multi-dimensional. Usually, this problem is overcome by presenting the potentials along two selected modes which are considered relevant reaction coordinates. We avoid this limitation by plotting the surfaces against time $t$, to obtain reaction energy profiles. These follow the optimal paths chosen by the wave function, unravelling them into a single dimension (see Fig. 5.5).
Fig. 5.5 **Energy surfaces and their diabatic populations.** The filled areas indicate the amount of diabatic population on each surface. The surfaces (dots) are coloured according to their mixing of electronic states. (a) The SF dynamics are not caused by conical intersections in the adiabatic PES. (b) Instead the vibronic mixing and super-exchange is sufficient to produce an avoided crossing at 80 fs of LE$^+$ and TT in the non-adiabatic TES causing rapid SF.
5.5 Simulation Results

We calculate the energy surfaces on-the-fly as the eigenvalues of the effective Hamiltonian $\mathbf{H}^{\text{eff}}(t)$ and potential $\mathbf{V}^{\text{eff}}(t)$

\[ H^{\text{eff}}_{(ij),(k,l)}(t) = \langle \phi_i(t) | \hat{\mathbf{H}} | \phi_k(t) \rangle | l \rangle, \quad (5.3) \]
\[ V^{\text{eff}}_{(ij),(kl)}(t) = \langle \phi_i(t) | \langle j | \hat{\mathbf{H}} - \hat{\mathbf{T}} | \phi_k(t) \rangle | l \rangle, \quad (5.4) \]

where $i, k$ index bath states and $j, l$ denote the electronic states. Since we simultaneously consider five different bath states $|\phi_i(t)\rangle$, as needed for strong exciton-phonon entanglement, $\mathbf{H}^{\text{eff}}(t) \in \mathbb{C}^{25 \times 25}$ yields 25 energy surfaces. Each $|\phi_i(t)\rangle$ relates to a strongly entangled superposition of elementary, localised phonon wave packets $|\varphi_j(x(t))\rangle$ (see Sec. 3.4). Fortunately, the wave function mostly populates only two surfaces (see Fig. 5.5a) which we will focus on in the following. Our method is basis free, independent on the choice of local oscillator wave functions, since we use $\mathbf{V}^{\text{eff}}(t)$ and $\mathbf{H}^{\text{eff}}(t)$ only. In contrast to the population and occupation dynamics we now look into the energetics of the dynamics (Fig. 5.5) which are revealed as changes of the energy level (dots), the overall population of each surface (fills), and even the mixing of diabatic electronic states (colour of fills) on the surfaces.

For each electronic state we can observe five energy surfaces (Fig. 5.5a), each caused by a different nuclear configuration. Oscillatory features are created by normal mode displacements and can be assigned to specific environments. As an example, the dominant oscillations with $\approx 20$ fs period visible in the highest PES of CT$^\pm$ are created by $A_{1,2}$ displacements tuning their energy levels (cf. Fig. 5.3b). Avoided crossings between energy surfaces indicate coupling between the respective diabatic states, accompanied by state mixing expressed in changing surface colour. The SF dynamics in the adiabatic PES (Fig. 5.5a) are evident as population transfer from the lowest LE$^+$ surface to the lowest TT surface. Since the population transfers between non-crossing surfaces, this displays the non-adiabatic nature of the dynamics.

The adiabatic PES of the populated TT (blue) stays consistently below the LE$^+$ PES (red, Fig. 5.5a), thus SF in DP-Mes should not be caused by a conical intersection as proposed for other SF systems [80, 86]. The crossings of the highest energy TT PES and the main LE$^+$ PES are not conical intersections and do not transfer populations, as they correspond to spatially separated and uncorrelated environmental states. Instead, SF is driven by an avoided crossing in the non-adiabatic TES (Fig. 5.5b) at 80 fs, caused by three main factors. First, the unoccupied TT TES is pushed above the LE$^+$ TES at 20 fs by $A_{12}$ and $B_{22}$, as indicated by correlations with their RC displacement and
excitation (see Fig. 5.6). Secondly, the TT is effectively coupled to the LE$^+$ resulting in the avoided crossing gap of 11 meV. The third factor is the lowering of TT through the avoided crossing which leads to population transfer onto TT.

The above time scales are found in the environment’s RC frequencies, reflecting properties of the collective motion, giving us more information about the underlying mechanisms. While the energy increase of the TT TES at 20 fs is caused by $\omega_{RC,A_1} \approx 1377 \text{ cm}^{-1} \sim 24 \text{ fs}$ and $\omega_{RC,B_1} \approx 1100 \text{ cm}^{-1} \sim 30 \text{ fs}$, the effective vibronic coupling depends on $B_2$ and $\omega_{B_1} \approx 400 \text{ cm}^{-1} \sim 83 \text{ fs}$, setting a longer time scale for SF (Fig. 5.3b,d). The slow reorganisation of $B_1$ increases the effective coupling, as half of the avoided crossing gaps, from 3 meV at 20 fs to 6 meV at 80 fs. Crucially, the $B_1$ modes also lead to the TT TES descent, slow enough in the Landau-Zener sense to minimise the residual LE$^+$ population on the upper surface, in contrast to the rapid crossing at 20 fs with no population transfer. Estimates based on the Landau-Zener formula for the diabatic transition probability predict a coupling of 10 meV which is encouragingly close to our result (see Sec. 5.6.5). This confirms that vibrationally mediated SF can be fast without the need for a conical intersection. We can furthermore exclude participation of the more direct path I via $A_2$, since its TT projected RC occupation rapidly drops, which can only happen if TT was populated through CT$^-$ (see Sec. 5.6.4).

While the PES exhibits that SF proceeds continuously downhill across an energy gap of 250 meV, thus driven towards TT as expected for exothermic reactions, the TES confirms that the dynamics proceed at constant energy. The correlation of electronic and bath dynamics shows that it is the sequence and interplay of multi-environment reorganisation and their respective time scales that create the conditions for the rapid super-exchange LE$^+ \rightarrow$ TT, overcoming the CT energy barrier by involving CT$^-$ only as a virtual state. This illustrates how multiple environments, their different collective time scales, and their effect on different types of dynamics are relevant in realistic molecules and that TTNS can reveal the mechanism.

### 5.6 Supporting Results

The following discussions are part of the supplementary information and investigate several previously mentioned aspects to more detail.
5.6 Supporting Results

5.6.1 Energy Surfaces

The SF dynamics mainly occupy two relevant energy surfaces, one with major LE$^+$ and the other with TT character, which we will focus our discussions on. The adiabatic PES (Fig. 5.6d) of TT is consistently below the LE$^+$ PES exhibiting the absence of any conical intersection. The dynamics of each PES are only slightly downhill with a mean reorganisation of 80 meV of LE$^+$ and 90 meV of TT. The non-adiabatic TES (Fig. 5.6a) exhibits almost iso-energetic dynamics at 2.06 meV with a central avoided crossing (AC) at 80 fs. Transforming the PES into the non-adiabatic states (Fig. 5.6b) we see a smooth descent from the LE$^+$ to the TT surface indicating the exothermic SF without an activation barrier. Rotating the TES into the adiabatic basis (Fig. 5.6c) we can identify the actual crossing of the two coupled surfaces. In the following we detail main observations leading to SF and compare them to environmental dynamics and RC properties to investigate the mechanism.

At 20 fs the unoccupied TT TES is pushed above the LE$^+$ (Fig. 5.6a) through interaction with the $B_{22}$ and $A_{12}$ environments, as confirmed by comparison with their TT-projected RC displacements (Fig. 5.6b). While a larger $\langle x_{RC} \rangle$ in $B_{22}$ raises the TT energy, the effect of $A_{12}$ is opposite as evident from the bottom three TT surfaces which move anti-parallel to the displacement. We can find similar timescales in the eigenfrequencies of the respective RCs of $\omega_{RC,A_{12}} \approx 1377 \text{ cm}^{-1} \sim 24 \text{ fs}$ and $\omega_{RC,B_{22}} \approx 1100 \text{ cm}^{-1} \sim 30 \text{ fs}$, confirming our observations. The AC at 20 fs with a gap
Fig. 5.7 Populations (upper) and environmental RC occupation dynamics (lower) of the 75 mode model for DP-Mes. The dynamics are equivalent to the full model (dotted) since only weakly coupled modes were removed. Adding weak dissipation to the 75 modes via broadening yields only $\approx 80\%$ TT (dashed).

of 6 meV is traversed rapidly by the TT, leading to almost no population exchange, while the AC at 80 fs with a gap of 12 meV seems to be the main driver of SF. The relatively weak coupling of 3 meV (half AC gap) is a result of slow $B_{11}$ reorganisation which happens on a longer $\omega_{B_{1}} \approx 400 \text{ cm}^{-1} \sim 83 \text{ fs}$ timescale leading to a larger effective vibronic coupling of 6 meV at 80 fs. Also the lowering of the TT TES is correlated with the excitation of the $B_{11}$ RC, which leads to traversing the crossing at the same time as the effective vibronic coupling is maximised. The crossing velocity of the two surfaces is low enough to keep the majority of initial LE$^+$ population on the lower surfaces (see Section 5.6.5).

The transfer to TT happens through change of character of the lower TES as the TT surface crosses. In the adiabatic PES it corresponds to non-adiabatic transitions between surfaces.

Remarkably, it is not (only) the Rabi-populated CT$^+$ state leading to SF since the TES TT surface does not exhibit corresponding oscillatory features. This is supported by the exclusion of the $A_2$ pathway in Section 5.6.4.

Effective couplings around 6 meV have been reported previously for tetracene dimers [4], highlighting the possibility for quantitative predictive power.

### 5.6.2 Dynamics with fewer modes

In order to evaluate to what extent models with fewer modes can give reasonably accurate results, we simulated a model based on 75 modes containing 99.7% of the
Table 5.1 Reaction coordinate frequencies and couplings of the 75 mode model

<table>
<thead>
<tr>
<th>Irrep.</th>
<th>$\omega$/cm$^{-1}$</th>
<th>$\lambda$/cm$^{-1}$</th>
<th>Irrep.</th>
<th>$\omega$/cm$^{-1}$</th>
<th>$\lambda$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1,1}$</td>
<td>902.1</td>
<td>1446.1</td>
<td>$A_{1,2}$</td>
<td>1377.5</td>
<td>4012.0</td>
</tr>
<tr>
<td>$B_{1,1}$</td>
<td>447.9</td>
<td>1845.1</td>
<td>$B_{1,2}$</td>
<td>225.4</td>
<td>628.1</td>
</tr>
<tr>
<td>$B_{2,1}$</td>
<td>1189.9</td>
<td>1073.2</td>
<td>$B_{2,2}$</td>
<td>1085.6</td>
<td>959.9</td>
</tr>
<tr>
<td>$A_{2}$</td>
<td>416.3</td>
<td>545.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

coupling strength of the 252 mode model. The calculations of the truncated Hamiltonian, including only modes $n$ with $\lambda_n > 100$ cm$^{-1}$ (similar to Table 5.4), generates very similar dynamics (Fig. 5.7). This observation suggests that there is only little qualitative difference between the 252 modes and 75 modes model which is also confirmed by the parameters of the RCs in Table 5.1. Nevertheless there is only minor speed-up of calculations due to shorter chains, as the main scaling bottleneck is the ER tree network which has to renormalise the same amount of entanglement.

We studied the effect of an external dissipative environment on the SF dynamics by broadening the vibrational spectra. We broaden each vibrational mode by 10 cm$^{-1}$ with a Lorentzian lineshape while conserving the reorganisation energy. The resulting spectral densities are mapped onto chain environments using orthogonal polynomials as described in Ref. [104]. We truncate the semi-infinite chains to a length $L = 70$ such that the exciton dynamics are unaffected by reflections from the end of the chains. The resulting dynamics show a lower TT yield of 80% along with a three times larger LE$^+$ population of 15%. The absence of further kinetic energy seems to limit SF to this upper value. However, as soon as the reflection from the end of the chains impact on the system past 1 ps, the TT increases again by a few percent. This suggests, that even after an equilibrium is reached, excitation of the environment, such as heat or a push pulse, could increase the yield of fission.

The super-exchange character of $\text{LE}^- \xrightarrow{B_1} \text{CT}^- \xrightarrow{B_1} \text{TT}$ is confirmed by the appearance of $\text{Im}(\rho_{\text{TT,LE}^-})$ and the large static coherence $\text{Re}(\rho_{\text{TT,LE}^-})$ (Fig. 5.8). The latter manifests as a coherent superposition of TT, LE$^-$, and CT$^-$ in the long-time state ($> 300$ fs). The mixture of this strong vibronic (dressed) state is modulated by $B_1$ and $A_1$ (Fig. 5.7c). The von Neumann entropy $S$ of the RDM increases until 90 fs which shows the strong non-adiabatic character of the SF dynamics (see Fig. 5.8). At this point the electronic state is maximally distributed among LE$^\pm$, CT$^\pm$, and TT. As the
Fig. 5.8 Coherences and entropy of the 75 mode model. Amongst the dynamic coherences $\text{Im}(\rho_{ij})$ (a) and the static coherences $\text{Re}(\rho_{ij})$ (b), $\rho_{TT,LE^-}$ is the strongest as caused by the super-exchange via $B_1$. (c) The system von Neumann entropy $S$ increases initially due to strong state mixing but subsequently decreases indicating a purification of the overall state.
5.6 Supporting Results

Fig. 5.9 Initial time Rabi-like dynamics. (a) The $\text{LE}^+ \xrightleftharpoons{B_2} \text{LE}^-$ Rabi oscillations are equally strong in $B_{21}$ and $B_{22}$ and vanish already after 15 fs but create $\approx 20\% \text{LE}^-$. (b) $\text{LE}^+ \xrightleftharpoons{B_1} \text{CT}^+$ undergoes Rabi dynamics mainly with $B_{11}$, lasting for 40 fs. The low yield of 8\% indicates strong detuning.

TT population increases subsequently, $S$ decreases again due to purification of the state and demixing with the environment.

5.6.3 Rabi Dynamics

The $< 20$ fs dynamics are dominated by very fast vacuum Rabi-like oscillations. However, correlating system and environment observables, such as $\langle n_{RC} \rangle$ (see Fig. 5.3) to visualise these is indicative, since expectation values are averages over microscopic states of competing dynamics, such as environmental reorganisation. By taking $\langle n \rangle$ only with respect to one of the five effective (microscopic) bath states $\langle \phi_j | \hat{n} | \phi_j \rangle$ we can single out one particular type of process. The system tensor wave function $A \in \mathbb{C}^{D \times d_s}$ tells which pairs of system and bath states are dominant.
Simulations of Singlet Fission in DP-Mes

The Rabi dynamics $\text{LE}^+ \xrightleftharpoons{B_1} \text{CT}^+$ are happening between $|\text{LE}^+, \phi_1\rangle$ and $|\text{CT}^+, \phi_3\rangle$, as evident from the anti-parallel dynamics of $\rho(\text{CT}^+)$ and $\langle \phi_3 | \hat{n}_{B_{1,RT}} | \phi_3 \rangle$ (Fig. 5.9b). We can see that $B_{1,2}$ only participates to $2\%$ while $B_{1,1}$ has a contribution of $98\%$. Since the driving is very off-resonant and comparably weak, with a RC frequency $\omega = 450 \text{ cm}^{-1}$, an $\text{LE}^+ - \text{CT}^+$ energy gap $\Delta \approx 5500 \text{ cm}^{-1} - 6500 \text{ cm}^{-1}$, and coupling $\lambda \approx 1350 \text{ cm}^{-1}$, the Rabi frequency $\Omega_R$ is very large ($T \approx 5.1 \text{ fs} \rightarrow \Omega_R \approx 6500 \text{ cm}^{-1}$). It should be noted that in this regime the counter-rotating terms cannot be neglected such that the usual rotating-wave approximation (RWA) is invalid. Thus we obtain the Rabi frequency as 

$$\Omega_R = \Delta \left( 1 + \frac{\lambda^2}{\Delta^2} \right). \quad (5.5)$$

The maximum population on $\text{CT}^+$ can only reach $8\%$ as confirmed by

$$P(\text{CT}^+) = \frac{\lambda^2}{\Omega_R^2}. \quad (5.6)$$

The process $\text{LE}^+ \xrightleftharpoons{B_2} \text{LE}^-$ involving $|\text{LE}^+, \phi_1\rangle$ and $|\text{LE}^-, \phi_2\rangle$ is strongly damped and lasts only for 2 periods, while rapidly generating $\approx 20\%$ of $\text{LE}^-$ (Fig. 5.9a). Here the two split environments are equally participating with $55\% (B_{2,1})$ and $45\% (B_{2,2})$, as seen by the initial value of the occupation. Since the detuning is much lower ($\omega \approx 1100 \text{ cm}^{-1}, \Delta \approx 2314 \text{ cm}^{-1} - 3950 \text{ cm}^{-1}, \lambda \approx 860 \text{ cm}^{-1}$) the expected Rabi frequency is lower ($\Omega_R \approx 2633 \text{ cm}^{-1} - 4137 \text{ cm}^{-1}$). The maximum expected $\text{LE}^-$ population ranges within $11\% - 4\%$ per environment, which agrees with the actually achieved $23\%$.

### 5.6.4 Exclusion of $A_2$ pathway

We can confidently prove that pathway I coupled via the $A_2$ environment is not contributing substantially to the observed SF dynamics by looking at the TT projected occupation

$$\langle \hat{n}_{RC,A_2,TT} \rangle = \langle \Psi | P_{TT} \hat{n}_{RC,A_2} | \Psi \rangle, \quad (5.7)$$

where $P_{TT} = |TT\rangle \langle TT|$ is the projector onto TT. Since the vibrationally mediated transport $\text{CT}^+ \rightarrow \text{TT}$ can only happen through the excitation of $A_2$ as $|\text{CT}^+\rangle |0\rangle_{A_2} \rightarrow |\text{TT}\rangle |1\rangle_{A_2}$, while pathway II via $\text{LE}^- \rightarrow \text{CT}^- \rightarrow \text{TT}$ happens at $|0\rangle_{A_2}$, the magnitude of this TT projected occupation gives direct evidence of how much TT has come via pathway I. Initially, $\langle \hat{n}_{RC,A_2,TT} \rangle \approx 1$ indicates that almost all TT was generated through
Fig. 5.10 $A_2$ RC occupation projected onto TT. Most of the initial $<10\,\text{fs}$ TT was generated via pathway I as indicated by the large $\langle \hat{n}_{RC,A_2} \rangle > 0.7$. At the equilibrium state $\langle \hat{n}_{RC,A_2} \rangle \approx 0.07$ shows that only 7% of the total TT came from path I, while the rest has taken path II.

path I. Subsequently this occupation drops rapidly, indicating a larger population of $|\text{TT}\rangle \langle 0|_{A_2}$ which can only happen via path II. The final value $\langle \hat{n}_{RC,A_2} \rangle \approx 0.07$ shows that 93% of TT has been generated through path II.

5.6.5 LE$^+ \to$ TT as Landau-Zener transition

We can interpret the passage through the avoided crossing in terms of a Landau-Zener passage which allows the adiabatic transition LE$^+ \to$ TT if the decrease in energy gap is slow enough. Based on the Landau-Zener formula for the probability of diabatic transition

$$P_D = \exp \left( -2\pi \frac{a^2}{\hbar |\alpha|} \right),$$

(5.8)

with $a = 6\,\text{meV}$ being the effective coupling between the surfaces and $\alpha = 0.727\,\text{meV}/\text{fs}$ the rate of change of the energy gap, we can calculate a 62% transition probability which is not properly matching the observed kinetics. The formula would predict a coupling of $10\,\text{meV}$ to yield the expected 25% transition probability. Given that the Landau-Zener formula is based on multiple assumptions which are all violated in these real dynamics, such as a time-independent diabatic coupling, linearly varying energy gap, and the perturbation parameter of the Hamiltonian being a linear function of time, it is ensuring that the found and expected effective coupling are at a comparable order of magnitude.
5.7 Conclusions

For this work we developed our TTNS method which can simulate the non-perturbative dynamics of large, heterogeneous, bosonic open quantum system models with multiple environments in terms of a closed quantum system. We improved the TTNS with entanglement renormalisation tensors as a key technique to enable the simulation of models with a large number of environments. To promote MPS to the presented TTNS a time-evolution based on the TDVP was essential to correctly update the ER-tensors and improve upon TEBD. We have successfully shown how TTNS can be interfaced with \textit{ab initio} methods, such as DFT, by borrowing machine learning techniques and deriving an optimal Hamiltonian, automated and objectively based on clustering. This identification of individual environments yields an optimal classification with controllable error in the employed approximation. The subsequent chain transformation reduces computational effort without compromising accuracy by harnessing the underlying entanglement topology within an independent environment. The obtained reaction coordinates provide intuitive insight into characteristic timescales of their environments. We have developed a unique approach to calculate and visualise the relevant energy surfaces, on-the-fly, exactly as they are experienced by the quantum system’s dynamics, with time as generalised reaction coordinate, avoiding the obstacles of representing surfaces in extreme multi-dimensional space. This concept inherently keeps track of multiple environmental states as they are required by and essential to non-Born-Oppenheimer dynamics. With DP-Mes as a case study, we have harnessed these energy surfaces to elucidate the mechanism behind SF and to understand the combined and simultaneous action of multiple environments leading to the observed dynamics. This shows how our method can support computational materials discovery in combination with well established \textit{ab initio} electronic structure calculations. The methods we outlined in this chapter are not restricted to singlet fission, but can be applied to a multitude of condensed matter systems ranging from simple organic molecules to polymers, molecular complexes, cavity QED, and circuit QED, amongst others.
Appendix 5.A  Methods

The following section is reproduced with D. H. P. Turban’s permission and was, together with parts of Sec. 5.2, his contribution to the submitted manuscript.

5.A.1  DFT

All DFT calculations were performed with the NWChem electronic structure code in vacuum [123]. The ground-state structure and vibrational modes were obtained employing analytical Hessians at the cc-PVDZ/B3LYP level of theory. Excited state energies and forces (corresponding to the diagonal elements of $W$) for LE$^\pm$ and CT$^\pm$ were calculated from (linear-response) TD-DFT gradients at the cc-PVDZ/LC-BLYP level of theory. The long-range corrected functional is required to correctly describe the $S_1$ state of pentacene as well as the states with charge-transfer character. An optimised range-separation parameter $\mu = 0.29$ was used in the LC-BLYP functional. This choice gives a good description of the energy of the first excited singlet of the pentacene molecule [141]. For TT the quintet state (total spin 2) was used as a proxy for the purpose of calculating energy and forces. The frontier molecular orbitals at the cc-PVDZ/LC-BLYP level were also used as inputs for the evaluation of the off-diagonal couplings.

Off-diagonal couplings and symmetries

To first order in nuclear displacements, the matrix elements of the diabatic potential matrix between electronic states $i$ and $j$ are given by [143]

$$ W_{n,ij} = \langle i | \frac{\partial \hat{H}_{el}}{\partial Q_n} | j \rangle, \quad (5.9) $$

where the $Q_n$ represent normal-mode coordinates of the ground state. The diagonal elements are simply the adiabatic forces (expressed in terms of normal coordinates), which we obtain directly from DFT.

For the purposes of the symmetry analysis and evaluation of the off-diagonal coupling vectors we employ an approximate multi-reference description of the electronic states, following Ref. [112]. This uses a small active space comprised of the four orbitals $h_A$, $h_B$, $\ell_A$, $\ell_B$, namely the monomer-localised HOMOs/LUMOs corresponding to the two pentacene units that make up DP-Mes (see Fig. 5.11). As can be seen from the
Fig. 5.11 DP-Mes structure with symmetry elements of the $D_{2d}$ point group, and frontier molecular orbitals. Note that extremal hydrogens of mesitylene side-groups weakly break the point group symmetry. However, this is irrelevant for the low-energy excitations since the frontier orbitals firmly reside on the pentacene units.

In the figure this set of localised orbitals is already orthogonal due to symmetry, meaning that a separate Löwdin orthogonalisation step is not necessary. In this set the ground state can be represented as the single determinant $|h_A \alpha h_A \beta h_B \alpha h_B \beta \rangle$, where $\alpha$ and $\beta$ label the electron spins. Furthermore, we have the locally excited states of each pentacene unit:

$$\text{LE}_A = \frac{1}{\sqrt{2}} \left[ |h_A \alpha \ell_A \beta h_B \alpha h_B \beta \rangle - |h_A \beta \ell_A \alpha h_B \beta h_B \beta \rangle \right], \quad (5.10)$$

$$\text{LE}_B = \frac{1}{\sqrt{2}} \left[ |h_A \alpha h_A \beta h_B \ell_B \beta | - |h_A \alpha h_A \beta h_B \beta \ell_B \alpha | \right], \quad (5.11)$$

as well as the corresponding CT states where the excited electron is transferred to the other pentacene unit, respectively:

$$\text{CT}_A = \frac{1}{\sqrt{2}} \left[ |h_A \alpha \ell_B \beta h_B \alpha h_B \beta | - |h_A \beta \ell_B \alpha h_B \beta h_B \beta | \right], \quad (5.12)$$

$$\text{CT}_B = \frac{1}{\sqrt{2}} \left[ |h_A \alpha h_A \beta h_B \ell_A \beta | - |h_A \alpha h_A \beta h_B \beta \ell_A \alpha | \right]. \quad (5.13)$$
Table 5.2 Excitation energies and symmetry classification of electronic states.

<table>
<thead>
<tr>
<th>state</th>
<th>E (eV)</th>
<th>irrep</th>
<th>E</th>
<th>2S_4</th>
<th>C_2</th>
<th>2C'_2</th>
<th>2σ_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS</td>
<td>0.00</td>
<td>A_1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>TT</td>
<td>1.83</td>
<td>A_1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>LE^+</td>
<td>2.07</td>
<td>B_2</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
</tr>
<tr>
<td>LE^-</td>
<td>2.20</td>
<td>A_1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
</tr>
<tr>
<td>CT^+</td>
<td>2.75</td>
<td>A_2</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>CT^-</td>
<td>2.76</td>
<td>B_1</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
</tr>
</tbody>
</table>

To obtain states that transform as irreducible representations of the point group we need to perform an (anti)symmetrisation step:

\[ \text{LE}^\pm = \frac{1}{\sqrt{2}} [\text{LE}_A \pm \text{LE}_B], \quad (5.14) \]
\[ \text{CT}^\pm = \frac{1}{\sqrt{2}} [\text{CT}_A \pm \text{CT}_B]. \quad (5.15) \]

Finally, the correlated triplet pair TT can be expressed as:

\[ \text{TT} = \frac{1}{\sqrt{3}} [|h_A \alpha \ell_A \alpha h_B \beta \ell_B \beta| + |h_A \beta \ell_A \beta h_B \alpha \ell_B \alpha| - \frac{1}{2} (|h_A \alpha \ell_A \beta h_B \alpha \ell_B \beta| + |h_A \alpha \ell_A \beta h_B \beta \ell_B \alpha| + |h_A \beta \ell_A \alpha h_B \beta \ell_B \alpha| + |h_A \beta \ell_A \alpha h_B \alpha \ell_B \beta|)]. \quad (5.16) \]

Using this picture one can now classify the electronic states according to irreducible representations of the point group. First, one considers how the minimal orbital basis \( h_A, h_B, \ell_A, \ell_B \) transforms under the symmetry operations of \( D_{2d} \). For example a \( C_2 \) rotation about the principle axis induces the mapping \( h_A \rightarrow -h_A, h_B \rightarrow -h_B, \ell_A \rightarrow -\ell_A \) and \( \ell_B \rightarrow -\ell_B \). By considering these transformations under all symmetry operations and substituting into the minimal-basis wave functions of the electronic states one obtains the right hand part of Table 5.2. The sign changes of the wave functions under the symmetry operations then directly determine the respective symmetry label.

To evaluate the diabatic potential matrix \( W \) to first order we can now go ahead and substitute the frontier orbital representations of the electronic states. Application of the Slater-Condon rules and some algebra then yields the following off-diagonal
Table 5.3 Product table of 1D-irreps of $D_{2d}$.

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$B_1$</td>
<td>$B_2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$B_2$</td>
<td>$B_1$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$B_1$</td>
<td>$B_2$</td>
<td>$A_1$</td>
<td>$A_2$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$B_2$</td>
<td>$B_1$</td>
<td>$A_2$</td>
<td>$A_1$</td>
</tr>
</tbody>
</table>

coupling contributions:

\[
W_{(\text{LE}^{+}\text{LE}^{-})} = \frac{1}{2} \left[ W(h_B h_B) - W(h_A h_A) - W(\ell_B \ell_B) + W(\ell_A \ell_A) \right] \tag{5.17}
\]

\[
W_{(\text{CT}^{+}\text{CT}^{-})} = \frac{1}{2} \left[ W(h_B h_B) - W(h_A h_A) + W(\ell_B \ell_B) - W(\ell_A \ell_A) \right] \tag{5.18}
\]

\[
W_{(\text{LE}^{+}\text{CT}^{+})} = W(\ell_A \ell_B) - W(h_A h_B) \tag{5.19}
\]

\[
W_{(\text{LE}^{-}\text{CT}^{-})} = W(\ell_A \ell_B) + W(h_A h_B) \tag{5.20}
\]

\[
W_{(\text{TT} \text{CT}^{\pm})} = \frac{\sqrt{3}}{2} \left[ W(\ell_A h_B) \pm W(h_A \ell_B) \right] \tag{5.21}
\]

The matrix elements $W_{(ab)}$ between single orbitals $a, b$ are now simply the Coulombic forces on the nuclei due to the overlap density $a(r)b(r)$. It should be pointed out that the first-order coupling vectors cannot have contributions from two-electron matrix elements since the electron-electron Coulomb interaction is independent of the nuclear coordinates and vanishes when taking the derivative in Eq. (5.9). Any vibrational mode can only give a non-zero contribution to the coupling between two electronic states if the product of the respective irreducible representations yields the totally symmetric representation $A_1$. For example modes contributing to the coupling between $\text{LE}^{+}$ ($B_2$) and $\text{CT}^{+}$ ($A_2$) necessarily transform as $B_1$ (see Fig. 5.12 and Table 5.3).

**Limitations of DFT**

There are a number of limitations of the methods and approximations described. These include treating the normal modes in the harmonic regime, and only accounting for the coupling between vibrations and electronic states to first order in the nuclear displacements. Furthermore, the evaluation of the off-diagonal elements of the potential matrix is based on a description of the electronic states in terms of a small active space of frontier-orbitals only. This is necessary to correctly capture the spin-structure of the states involved in fission, at the expense of the representational power of the
Fig. 5.12 The states relevant for SF and their symmetries in the point group $D_{2d}$. The lines indicate the vibrational coupling and the symmetry of the corresponding modes. The grey couplings involve 2 electron interactions and are vanishingly small.

basis used. In addition, these wave functions are constructed from Kohn-Sham orbitals which are eigenfunctions of the non-interacting Kohn-Sham system rather than the full electronic Hamiltonian. Since these orbitals are expressed in terms of Gaussian basis functions centred on the nuclei we also do not capture Pulay terms when evaluating the off-diagonal elements of $W$ according to Eq. (5.9). Finally, it should be noted that CT energies from TD-DFT, while not severely underestimated thanks to the use of range-separation, instead come out quite significantly higher than LE. It can be suspected that the lack of diffuse functions in the basis set and the linear-response nature of the TD-DFT calculations play a role here. Both hamper the ability to capture the intra-molecular relaxation of a CT configuration.

Given all these limitations, our parametrisation of the vibronic coupling Hamiltonian should be considered semi-quantitative.
5.A.2 Tensor Network States

To prepare the linear vibronic DP-Mes Hamiltonian for the TTNS simulations, the vibrational modes were clustered to independent environments by using a weighted k-means algorithm [9]. These environments were mapped onto chain Hamiltonians with the orthogonal polynomials transformation [26].

The model was simulated with a TTNS as depicted in Fig. 5.2, incorporating entanglement renormalisation (ER) tensors connecting the vibrational chain environments to the excitonic states and using an optimised boson basis (OBB) to allow for a large and expandable Fock basis. The time-evolution is performed in the time-dependent variational principle (TDVP) [55] to simulate exciton-phonon dynamics at zero temperature with no initial environmental excitations at a time step of 0.33 fs. Details about the TDVP algorithm we have developed for the TTNS evolution are given in the Sec. 3.2.5 and further background can be found in Refs. [55, 75, 104, 106, 116]. We keep 100 bosonic Fock states per vibrational mode. The dynamics converged sufficiently for an OBB dimension of 40, maximum TTNS bond dimension $D$ between ER-nodes of $D_{\text{Node, max}} = 80$, while along the chains $D_{\text{Chain, max}} = 30$ was appropriate. Thus we cover a Hilbert space of $10^{500}$ states using only $10^7$ parameters. Energy surfaces were calculated from the effective Hamiltonian and effective potential of the system tensor. Further computational details are provided in Sections 3.2, 3.3, and 3.4.
Appendix 5.B  Model parameters

After clustering we obtain the following coupling matrices for respective environments

\[
\begin{align*}
W_{A_1,1} &= -\begin{pmatrix} 0 & 0.45 & 0.38 \cr & 0.57 & 0.57 \end{pmatrix}, & W_{A_1,2} &= -\begin{pmatrix} 0.75 & 0.3 \cr & 0.29 & 0.37 \cr & & 0.37 \end{pmatrix}, \\
W_{A_2} &= -\begin{pmatrix} 0 & 1 \cr & 0 \cr & 1 & 0 \cr & & 0 \end{pmatrix}, & W_{B_1,1} &= -\begin{pmatrix} 0 & 0 & 0 \cr & 0 & 0 \cr & & 0 \cr & & & 0.63 \cr & & & 0.26 \cr & & & 0 \end{pmatrix}, \\
W_{B_1,2} &= \begin{pmatrix} 0 & 0 & 0 \cr & 0 & -0.33 \cr & & 0 \cr & & -0.9 \cr & & 0 \cr & & & 0.28 \cr & & & -0.9 \cr & & & 0 \end{pmatrix}, \\
W_{B_2,1} &= -\begin{pmatrix} 0 & 0 & 0.86 \cr & 0.86 & 0 \cr & & 0.52 \cr & & 0.52 \end{pmatrix}, & W_{B_2,2} &= \begin{pmatrix} 0 & 0 & -0.86 \cr & -0.86 & 0 \cr & & 0 \cr & & 0.52 \cr & & 0.52 \end{pmatrix}.
\end{align*}
\]

The modes assigned to the environments together with their frequencies and couplings are given in Table 5.4. In Table 5.5 we give the frequencies and coupling of the first sites, the reaction coordinates (RC) of each environment after chain transformation.
Table 5.4 All modes containing at least 90% of the total coupling.

<table>
<thead>
<tr>
<th>No.</th>
<th>( \omega/\text{cm} )</th>
<th>( \lambda/\text{cm} )</th>
<th>No.</th>
<th>( \omega/\text{cm} )</th>
<th>( \lambda/\text{cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1,1} )</td>
<td>28</td>
<td>129.8</td>
<td>398.5</td>
<td>40</td>
<td>259.5</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>269.2</td>
<td>479.3</td>
<td>60</td>
<td>471.3</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>579.6</td>
<td>-712.3</td>
<td>88</td>
<td>613.7</td>
</tr>
<tr>
<td></td>
<td>98</td>
<td>706.0</td>
<td>495.3</td>
<td>146</td>
<td>991.7</td>
</tr>
<tr>
<td></td>
<td>178</td>
<td>1190.0</td>
<td>-175.4</td>
<td>200</td>
<td>1339.6</td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>1464.6</td>
<td>-270.9</td>
<td>228</td>
<td>1469.2</td>
</tr>
<tr>
<td></td>
<td>236</td>
<td>1505.6</td>
<td>-326.3</td>
<td>260</td>
<td>1595.6</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>1654.6</td>
<td>-282.4</td>
<td>271</td>
<td>1692.1</td>
</tr>
<tr>
<td>( A_{1,2} )</td>
<td>116</td>
<td>805.2</td>
<td>1094.8</td>
<td>158</td>
<td>1036.0</td>
</tr>
<tr>
<td></td>
<td>174</td>
<td>1164.9</td>
<td>536.7</td>
<td>182</td>
<td>1219.4</td>
</tr>
<tr>
<td></td>
<td>186</td>
<td>1232.4</td>
<td>-850.0</td>
<td>190</td>
<td>1265.1</td>
</tr>
<tr>
<td></td>
<td>192</td>
<td>1271.4</td>
<td>1010.4</td>
<td>208</td>
<td>1372.5</td>
</tr>
<tr>
<td></td>
<td>214</td>
<td>1426.0</td>
<td>1217.4</td>
<td>216</td>
<td>1445.3</td>
</tr>
<tr>
<td></td>
<td>256</td>
<td>1579.0</td>
<td>-2285.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_2 )</td>
<td>24</td>
<td>122.4</td>
<td>-206.8</td>
<td>38</td>
<td>248.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>302.3</td>
<td>323.4</td>
<td>66</td>
<td>493.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>726.3</td>
<td>136.2</td>
<td>112</td>
<td>783.1</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>873.7</td>
<td>-53.7</td>
<td>134</td>
<td>937.9</td>
</tr>
<tr>
<td>( B_{1,1} )</td>
<td>35</td>
<td>234.9</td>
<td>-148.4</td>
<td>39</td>
<td>250.6</td>
</tr>
<tr>
<td></td>
<td>61</td>
<td>479.2</td>
<td>-1157.9</td>
<td>65</td>
<td>484.9</td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>720.8</td>
<td>493.0</td>
<td>111</td>
<td>782.7</td>
</tr>
<tr>
<td></td>
<td>133</td>
<td>921.5</td>
<td>389.9</td>
<td>135</td>
<td>939.6</td>
</tr>
<tr>
<td>( B_{1,2} )</td>
<td>25</td>
<td>122.6</td>
<td>410.0</td>
<td>49</td>
<td>301.7</td>
</tr>
<tr>
<td>( B_{2,1} )</td>
<td>41</td>
<td>268.2</td>
<td>-373.6</td>
<td>83</td>
<td>587.8</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>596.7</td>
<td>123.1</td>
<td>95</td>
<td>696.9</td>
</tr>
<tr>
<td></td>
<td>119</td>
<td>828.6</td>
<td>-131.1</td>
<td>159</td>
<td>1036.0</td>
</tr>
<tr>
<td></td>
<td>173</td>
<td>1140.8</td>
<td>126.3</td>
<td>177</td>
<td>1188.2</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>1231.1</td>
<td>141.8</td>
<td>187</td>
<td>1249.5</td>
</tr>
<tr>
<td></td>
<td>207</td>
<td>1347.7</td>
<td>-187.2</td>
<td>227</td>
<td>1466.9</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>1503.2</td>
<td>155.8</td>
<td>255</td>
<td>1576.6</td>
</tr>
<tr>
<td>( B_{2,2} )</td>
<td>21</td>
<td>108.5</td>
<td>-131.4</td>
<td>33</td>
<td>217.3</td>
</tr>
<tr>
<td></td>
<td>51</td>
<td>324.6</td>
<td>94.4</td>
<td>81</td>
<td>572.2</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td>688.6</td>
<td>174.8</td>
<td>113</td>
<td>797.6</td>
</tr>
<tr>
<td></td>
<td>181</td>
<td>1218.6</td>
<td>-146.7</td>
<td>191</td>
<td>1270.6</td>
</tr>
<tr>
<td></td>
<td>209</td>
<td>1384.4</td>
<td>202.7</td>
<td>215</td>
<td>1435.2</td>
</tr>
<tr>
<td></td>
<td>226</td>
<td>1464.7</td>
<td>-163.0</td>
<td>237</td>
<td>1522.9</td>
</tr>
<tr>
<td></td>
<td>265</td>
<td>1654.1</td>
<td>100.5</td>
<td>272</td>
<td>1692.1</td>
</tr>
</tbody>
</table>
Table 5.5 Reaction coordinate frequencies and couplings of the 252 mode model.

<table>
<thead>
<tr>
<th>Irrep.</th>
<th>$\omega$/cm$^{-1}$</th>
<th>$\lambda$/cm$^{-1}$</th>
<th>Irrep.</th>
<th>$\omega$/cm$^{-1}$</th>
<th>$\lambda$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1,1}$</td>
<td>903.4</td>
<td>1454.6</td>
<td>$A_{1,2}$</td>
<td>1377.3</td>
<td>4012.6</td>
</tr>
<tr>
<td>$B_{1,1}$</td>
<td>450.1</td>
<td>1851.5</td>
<td>$B_{1,2}$</td>
<td>225.4</td>
<td>628.2</td>
</tr>
<tr>
<td>$B_{2,1}$</td>
<td>1193.7</td>
<td>1083.9</td>
<td>$B_{2,2}$</td>
<td>1079.4</td>
<td>986.4</td>
</tr>
<tr>
<td>$A_{2}$</td>
<td>428.0</td>
<td>560.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The work in the preceding chapters presented the technical advances that were made to allow an in depth simulation and study of the quantum dynamics of excitons in light-harvesting complexes, as demonstrated at the example of an organic dimer. Nevertheless, an actual study of a natural light-harvesting complex is still mainly limited by insufficient accuracy or availability of model parameters due to the limitations of (TD)-DFT. While site energies and inter-chromophore couplings are reasonably well explored since they can be extracted from structures determined via X-ray diffraction crystallography, the vibronic coupling via phonon modes of the entire complex can only be determined in highly expensive TD-DFT calculations which usually scale exponentially in the number of atoms. Although there are already linear scaling DFT codes available, they are yet to be tested and applied to this type of systems.

Experimental studies of artificial light-harvesting are an interesting field because they have the potential to yield accurate results across a wide range in parameter space, from weak to strong coupling, avoiding approximations made in simulations or analytic approaches. There are a couple of groups investigating the chemical synthesis of molecular arrays to gain control over array length and topology, but their approaches are very limited in the possible mutual orientations of the chromophores. This lack of control means that it is nearly impossible to form perfect H- or J-aggregates or any arbitrary well defined state in between. Also the tuning of inter-chromophore coupling which depends on the mutual separation, is limited by the lengths and degrees of freedom of the frequently employed carbon bonds.
For these reasons we sought a different type of experimental system that is able to give full control over the chromophore system and even allows a precise design of the phonon environment. Superconducting circuits consist of inductances, capacitances, and resistances that exhibit quantum effects if they are made small enough. With these ingredients it is possible to manufacture a quantum harmonic oscillator or a qubit that can be prepared in any initial state and characterised precisely. Since the manufacturing mainly involves lithography at the micrometer scale, it is possible to precisely design the site energies and couplings. Flux lines give additional post-fabrication control over energies and can be used to fine-tune the system or to emulate a classical phonon environment of arbitrary power spectral density (PSD).

In this chapter we present work that was performed in close collaboration with Arno Bargerbos, Anton Potočnik, and Andreas Wallraff from ETH Zürich, who have strong expertise in superconducting circuits and were interested in applying their method to study mechanisms in light-harvesting. Since the study only involves classical environments, we performed the theoretical description and simulations with the master equation formalism, rather than the TTNS which is more suitable to study quantum environments. The aim of this work was to create a proof of concept, minimal artificial light-harvesting system that exhibits delocalised excitons with bright and dark states, energy mismatch and exciton trapping to study the effects of a phonon environment on exciton transport, termed noise assisted transport (NAT) [24, 29, 31, 57, 95, 100], that has only been proposed theoretically but has never been implemented experimentally.


F. A. Y. N. Schröder, A. W. Chin, and C. Creatore created the theoretical model, performed simulations, advised experiments, and interpreted the results. The group at ETH Zürich, including M. Collodo, S. Gasparinetti, Y. Salathe, and C. Eichler realised the model in a superconducting circuit with transmon qubits, performed all experiments and analysed the data. The figures in the following sections, where indicated, were produced by A. Potočnik and reproduced with his permission. The following text and interpretation is my original work and contribution to the publication.
6.1 Introduction

We present a model experimental system to study arrays of pigments, as found in photosynthetic complexes, and their interaction with an environment. Here we use engineered quantum circuits to study with unprecedented versatility and control, functional aspects of a minimal antenna-trap model. In particular, we experimentally demonstrate noise assisted transport (NAT) between quantum coherent sites disordered in energy for two environmental noise types. Additionally, we show that even under incoherent illumination, the system exhibits quantum coherent properties. The overall energy harvest is maximised for structured noise, similar to the phononic environment of photosynthetic complexes.

Our model circuit contains three transmon qubits, which behave like ideal two-level systems. We use two absorbers $Q_1, Q_2$, and a target $Q_3$ coupling to an energy trapping resonator (see Fig. 6.1). The waveguide excites only the symmetric, bright state. We measure the power spectral density (PSD) of re-emitted and extracted photons to characterise the energy transport.

In the following Section 6.2 we will first cover the model Hamiltonian proposing a minimal light-harvesting system, together with a characterisation of its implementation in terms of a circuit of superconducting qubits. Afterwards, we will describe how measurements can be simulated with the Lindblad master equation and how the relevant observables, such as currents and spectra are calculated (Sec. 6.3). In Section 6.4 we present measurements and simulations, where possible, to assess the performance of the proposed light-harvesting system and the suitability of the superconducting circuit. Finally, in Section 6.5 we summarise our insights and propose further directions.

6.2 Model Hamiltonian and characterisation

The proposed model Hamiltonian that corresponds to Fig. 6.1 in the $Q_1, Q_2$ basis reads:

\[
H = \sum_{i=1}^{3} \left[ (\omega_i - \omega_l) \sigma_i^+ \sigma_i^- + \sum_{j<i} J_{ji} (\sigma_j^+ \sigma_i^- + \sigma_i^+ \sigma_j^-) \right] + \frac{\Omega_l}{2} (\sigma_{x,1} + \sigma_{x,2}) + (\omega_r - \omega_l) a^\dagger a + g_3 (a^\dagger \sigma_3^- + \sigma_3^+ a),
\]

(6.1)

where $\sigma^+$ and $\sigma^-$ are the raising and lowering operators for the qubits obeying commutation relations $[\sigma_i^+, \sigma_j^-] = \delta_{i,j}$, and $a^\dagger, a$ are the operators for the resonator, with
Artificial light-harvesting in superconducting qubits

Fig. 6.1 (a) Model of the light-harvesting system that is implemented in the superconducting circuit (b). The qubits $Q_1$ (red) and $Q_2$ (blue) are excited symmetrically by the waveguide between connection 1 and 2. The flux lines 3 and 5 allow tuning of the energy levels of $Q_1$ and $Q_2$. $Q_3$ (green) is coupled to $Q_2$ and emits any transferred excitation into the resonator at port 4. Figure used with permission of A. Potočnik.

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$ transition frequency</td>
<td>$\omega_1/2\pi$</td>
<td>6.28365 GHz</td>
</tr>
<tr>
<td>$Q_2$ transition frequency</td>
<td>$\omega_2/2\pi$</td>
<td>6.28365 GHz</td>
</tr>
<tr>
<td>$Q_3$ transition frequency</td>
<td>$\omega_3/2\pi$</td>
<td>6.182 GHz</td>
</tr>
<tr>
<td>Resonator frequency</td>
<td>$\omega_r/2\pi$</td>
<td>6.0092 GHz</td>
</tr>
<tr>
<td>Coupling between $Q_1$ and $Q_2$</td>
<td>$J_{12}/2\pi$</td>
<td>83.55 MHz</td>
</tr>
<tr>
<td>Coupling between $Q_2$ and $Q_3$</td>
<td>$J_{23}/2\pi$</td>
<td>33.4 MHz</td>
</tr>
<tr>
<td>Coupling between $Q_1$ and $Q_3$</td>
<td>$J_{13}/2\pi$</td>
<td>3.67 MHz</td>
</tr>
<tr>
<td>Coupling between $Q_3$ and the resonator</td>
<td>$g_3/2\pi$</td>
<td>70 MHz</td>
</tr>
<tr>
<td>Bright state decay rate</td>
<td>$\gamma_b/2\pi$</td>
<td>13 MHz</td>
</tr>
<tr>
<td>Resonator decay rate</td>
<td>$\kappa/2\pi$</td>
<td>75 MHz</td>
</tr>
<tr>
<td>Bright state Rabi rate</td>
<td>$\Omega_R$</td>
<td>11.8 MHz</td>
</tr>
<tr>
<td>Input field frequency</td>
<td>$\omega_{in}/2\pi$</td>
<td>6.3665 GHz</td>
</tr>
</tbody>
</table>

Table 6.1 System parameters used for simulations. All parameters are experimentally determined from spectroscopic measurements except $g$ and $\kappa$ which were adjusted within their experimental uncertainty.
commutator \([a, a^\dagger] = 1\). The Hamiltonian is already transformed into the rotating frame of the driving line of frequency \(\omega_l\) which drives each qubit at a Rabi frequency of \(\Omega_l\). The frequencies, inter-qubit couplings \(J_{ji}\) and the trap to resonator coupling \(g_3\) are presented in Table 6.1. The coupling \(J_{12}\) is chosen to be strong compared to any other couplings to hybridise \(Q_1\) and \(Q_2\) yielding delocalised symmetric and antisymmetric eigenstates. Since \(Q_1\) and \(Q_2\) are spatially close compared with the wavelength of the microwave (\(\approx 8\) mm), the qubits are always phase-coherently excited into the symmetric bright state, leaving the antisymmetric state dark. The trap \(Q_3\) should couple only weakly to \(Q_2\) to extract the excitons but not disturb the hybrids and subsequently channel the energy into the resonator.

Since the qubits \(Q_1\) and \(Q_2\) are taken to be in a strong coupling regime, it is more appropriate to use the Hamiltonian in the bright and dark basis, which are the ideal hybrids generated by \(J_{12}\) for \(\omega_1 = \omega_2\)

\[
H = \frac{(\omega_1 + J_{12} - \omega_l)}{\omega_b} \sigma_b^+ \sigma_b^- + \frac{(\omega_1 - J_{12} - \omega_l)}{\omega_d} \sigma_d^+ \sigma_d^- \\
+ (\omega_3 - \omega_l) \sigma_3^+ \sigma_3^- + (\omega_r - \omega_l) a^\dagger a + \frac{\Omega_R}{2} \sigma_{x,b} \\
+ \frac{J_{23}}{\sqrt{2}} (\sigma_b^+ \sigma_3^- + \sigma_3^+ \sigma_b^-) - \frac{J_{23}}{\sqrt{2}} (\frac{\sigma_d^+}{2} \sigma_3^- + \sigma_3^+ \frac{\sigma_d^-}{2}) + g_{34} (a^\dagger \sigma_3^- + \sigma_3^+ a)
\]  
(6.2)

where we used the transformation \(\sigma_b^\pm = (\sigma_1^\pm + \sigma_2^\pm)/\sqrt{2}\) and \(\sigma_d^\pm = (\sigma_1^\pm - \sigma_2^\pm)/\sqrt{2}\) that diagonalises the \(Q_1, Q_2\) system and use the bright state Rabi frequency \(\Omega_R = \sqrt{2}\Omega_l\). The transformation shows that \(J_{b3} = J_{23}/\sqrt{2}\) and \(J_{d3} = -J_{23}/\sqrt{2}\), so the trap is coupled to both, bright and dark state. It should be noted that \(\sigma_{b/d}\) do not fulfil standard qubit commutation relations but instead

\[
[\sigma_i^+, \sigma_j^-] = \frac{1}{2} (\sigma_{z,1} - \sigma_{z,2}) + \sigma_{z,2} \delta_{i,j},
\]  
(6.3)

since they are not fully independent.

### 6.2.1 Experimental characterisation

The sample as depicted in Fig. 6.1b is characterised by measuring the transmission from port 1 to 2 for different drive frequencies \(\nu\). The resulting transmission spectra in Fig.6.2 show that for resonant \(Q_1\) and \(Q_2\) we can obtain almost perfect hybridisation with negligible absorption into the dark state. The distance between bright and dark
state absorption is equivalent to twice the coupling $J_{12}$. Sweeping both energies such that either $|b\rangle$ or $|d\rangle$ are resonant with the trap state yields a splitting from which $J_{23}$ can be determined via $J_{b3}$ and $J_{d3}$.

To properly investigate NAT, we tune the trap into resonance with the dark state, which results in dark-trap hybrids $|d_1\rangle$ and $|d_2\rangle$. Although the trap is coupled to bright and dark states simultaneously, off-resonance with the former and resonance with the latter will minimise bright to trap and maximise dark to trap current. In this configuration and in the absence of noise, there will not be any current flowing into the trap and resonator, since only the bright state will be excited and the bright and dark state are decoupled. We simulate NAT by applying two different types of dephasing noise (see PSD in Fig. 6.2c) to $Q_2$ via its flux line to cause transitions between the bright and dark state. The noise is generated with arbitrary waveform generators from a Gaussian random number sequence. Only with applied noise, the trap can extract energy from the dark state and forward it to the resonator. The detuning between trap and resonator defines the radiative Purcell decay rate $\gamma_{\text{Pur}}$ which models the energy extraction rate.

Fig. 6.2 (a) Transmission spectra $|t_{21}(\omega)|$ measured at port 2 for coherent driving of frequency $\nu$ at port 1. The magnetic flux $\phi$ is varied such that $Q_1$ and $Q_2$ are kept in resonance while sweeping both from 6 GHz to 6.37 GHz. (b) Energy level diagram corresponding to setting $\phi = 60$ (grey vertical line in (a)) and (c) noise spectra applied to flux line 5. Figure used with permission of A. Potočnik.
Determining the correct model parameters as inputs for the Hamiltonian is more difficult than it might seem at first sight, since the measured spectra of the circuit are highly sensitive to all couplings. Therefore, inferring couplings and frequencies from the transmission spectrum (Fig. 6.2a) by measuring energy gaps and positions of avoided crossings yields highly unsatisfactory results. A better approach is to perform the same calibration steps in simulations, as they were taken to calibrate the qubit system. This involves simulating calibration spectra and optimising model parameters such that the simulated and measured calibration spectra agree. With this scheme we determined the parameters given in Table 6.1, which enabled us to simulate spectra with exceptionally high accuracy.

Before presenting results we will give a more in-depth description on how to calculate quantities that are measured, such as PSDs of transmitted or emitted spectra, or currents that represent the total transmitted power.

6.3 Deriving observables from the master equation

6.3.1 Lindblad master equation

In the limit of weak $J_{23}$ we can take the qubit Hamiltonian to be approximately diagonal and define the Lindblad master equation as

$$
\mathcal{L}[\rho] = -i[H, \rho] + \gamma_b(1 + n_{th})L[\sigma^-_b]\rho + \gamma_b n_{th} L[\sigma^+_b]\rho + \gamma_d(1 + n_{th})L[\sigma^-_d]\rho + \gamma_d n_{th} L[\sigma^+_d]\rho + \gamma_3(1 + n_{th})L[\sigma^-_3]\rho + \gamma_3 n_{th} L[\sigma^+_3]\rho + \frac{\gamma_\phi}{2} L[\sigma_{z,2}]\rho + \kappa L[a]\rho, 
$$

with the Lindblad superoperator

$$
L[O]\rho = \frac{1}{2}[O, \rho O^\dagger] + h.c.,
$$

and the decay rates $\gamma_b, \gamma_d, \gamma_3$ of bright, dark, and trap state due to a thermal occupation $n_{th}$ of the circuit, the dephasing rate $\gamma_\phi$ of $Q_2$ and the loss rate $\kappa$ of the resonator. Strictly taken, the dephasing term is in the wrong basis since it is formulated in the
Artificial light-harvesting in superconducting qubits

$Q_2$ basis which is not a good eigenbasis and should be expanded into

$$L[\sigma_{z,2}] \rightarrow L[\sigma_b^+\sigma_b^- + \sigma_d^+\sigma_d^-] + L[\sigma_b^+\sigma_d^-] + L[\sigma_d^+\sigma_b^-]. \quad (6.9)$$

Nevertheless, analytic and numeric evaluations of the bright to dark current $j_{bd}$ are equivalent for both terms, which is why we will stay with the simpler expression.

### 6.3.2 Currents

#### General derivation

With the above equations of motion of $\rho$, as defined by the Lindblad master equation, we can derive the transport properties of the artificial light-harvesting system from the current operator $\hat{j}$. Since these operators are not straightforward to derive, we will a brief outline here.

The net current $j$ of a site with particle number operator $\hat{N}$ can be calculated as the time-dependent change $\dot{\hat{N}} = \frac{d}{dt}\langle \hat{N} \rangle$

$$j = \dot{\hat{N}} = \text{Tr}\{ \dot{\hat{N}} \hat{\rho} \} = -i\langle [\hat{N}, \hat{H}] \rangle + \sum_i \frac{\Gamma_i}{2} \langle \hat{O}_i^\dagger [\hat{N}, \hat{O}_i] + h.c. \rangle \quad (6.10)$$

where we used that $\dot{\hat{\rho}} = \mathcal{L}[\hat{\rho}]$ with time-independent and hermitian $\hat{N}$. For a steady-state $\rho_{ss}$ we have no net currents such that $j = 0$, which means that the individual currents cancel. Therefore it is important to find their explicit contributions in order to get non-zero and meaningful expectation values.

#### Coherent currents

We want to strengthen intuition about the coherent and incoherent contributions in the terms above which needs a closer look at specific commutators. For standard qubit operators $N = \sigma^+\sigma^-, \sigma_z = [\sigma^+, \sigma^-]$ we get the commutation relations

$$[N, \sigma_z] = 0, \quad (6.11)$$
$$[N, \sigma^\pm] = \pm \sigma^\pm. \quad (6.12)$$
$$[N, O + h.c.] = [N, O] - h.c., \quad (6.13)$$

where the last line only relies on hermitian $N$. Thus, the self-energy terms with $\sigma_z$ in the Hamiltonian do not contribute to the current, while dipolar terms such
as $\sigma_x = \sigma^+ + \sigma^-$ give $[N, \sigma_x] = \sigma^+ - \sigma^- = i\sigma_y$. All other currents generated by Hamiltonian terms therefore must originate from coherent coupling terms, such as for trap-resonator coupling

$$j_{3r} = -i \langle \sigma_3 a + h.c. \rangle$$

(6.14)

$$= -i \langle g_3 (\sigma^+_3 a - a^\dagger \sigma^-_3) \rangle = 2 g_3 \text{Im} \langle \sigma_3^+ a \rangle ,$$

(6.15)

which is the imaginary part of the trap to resonator coherence multiplied by the coupling strength. This result immediately shows the coherent nature of this current, as it will vanish together with the coherence. Furthermore, the sign of the coherence determines the direction of current.

**Incoherent currents**

For the Lindblad operators we have

$$\frac{\Gamma_i}{2} \langle \hat{O}_i^\dagger[^{\hat{N}, \hat{O}_i} + h.c.] \rangle = \Gamma_i \text{Re} \langle \hat{O}_i^\dagger[^{\hat{N}, \hat{O}_i} \rangle ,$$

(6.16)

which can only depend on populations or the real part of coherences. This can be simplified, as an example for the trap decay $O_i = \sigma^-_3$ to

$$j_{3,\gamma_3} = -\gamma_3 (1 + n_{th}) \text{Re} \langle \sigma^+_3 \sigma^-_3 \rangle ,$$

(6.17)

Since this current only depends on the occupation and is generated by the incoherent decay operator $L[\sigma^-_3]$ we can identify it as incoherent current. This also holds for the other currents generated by Lindblad operators as a fundamental property.

**Currents for bright and dark state**

In the following we will state the currents that can be derived for the bright & dark state, and resonator, as these can be related to measurable quantities. The coherent
currents for $N_b$ are found as

$$j_{b,H} = -i \langle [N_b, \frac{\Omega_R}{2} \sigma_{x,b} + J_{23}(\sigma_2^+ \sigma_3^- + \sigma_3^+ \sigma_2^-)] \rangle$$

$$= -i \langle \frac{\Omega_R}{2} (\sigma_2^+ - \sigma_2^- N_b) - J_{b3} \sigma_2^+ \sigma_2^- - h.c. \rangle$$

$$= \Omega_R \text{Im} \langle \sigma_2^+ - \sigma_2^- N_b \rangle - 2J_{b3} \text{Im} \langle \sigma_2^+ \sigma_2^- \rangle. \quad (6.18)$$

Although these terms seem fairly complex, their interpretation is straightforward. While the first term represents the usual absorption from the transmission line, the second term indicates a decrease in the bright population due to the transmission line, in case the bright state is occupied. The last term is negative for occupied $Q_2$ and positive for unoccupied $Q_2$, which represents the conditional transfer either into the trap state or into the bright state, respectively, depending on the state of $Q_2$.

The coherent currents for $N_d$ are

$$j_{d,H} = \Omega_R \text{Im} \langle \sigma_2^+ N_b \rangle - 2J_{d3} \text{Im} \langle \sigma_d^+ \sigma_2^- \rangle, \quad (6.19)$$

where the first term is linked to the term in the bright state current, indicating that there is a third order process that allows population of the dark state through the bright state through the coherent excitation into a doubly excited state.

The incoherent current due to the dephasing induced by the flux line $\gamma \phi L[\sigma_z]$ is

$$j_{b,\phi} = \frac{\gamma \phi}{2} \langle \sigma_2^+ [N_b, \sigma_2^-] + h.c. \rangle = \frac{\gamma \phi}{2} \langle N_d - N_b \rangle = -j_{d,\phi}, \quad (6.20)$$

depends only on population differences and exhibits the noise assisted transport. The decay current of the bright state is

$$j_{b,\gamma_b} = \gamma_b \text{Re} \langle \sigma_2^+ [N_b, \sigma_2^-] \rangle = \gamma_b \text{Re} \langle (N_d - N_b) N_b \rangle, \quad (6.21)$$

which agrees with the higher order process found in the coherent excitation.

For the resonator we already calculated the coherent current as

$$j_{r3} = -j_{3r} = 2g_3 \text{Im} \langle a^+ \sigma_3^- \rangle, \quad (6.22)$$

while we obtain for the incoherent decay

$$j_{r,\kappa} = -\kappa \text{Re} \langle N_r \rangle. \quad (6.23)$$
These currents can be directly related to the integrated output power spectra of the

### 6.3.3 Spectral features

Experimentally it is possible to measure power spectra of the bright state and resonator emission. The calculation of respective power spectra involves Fourier transforms of correlation functions which have been derived previously in the framework of input-output theory (see Gardiner and Zoller [47, ch. 5] and [46] for details). We will build upon this formalism to connect the currents derived above with the integrated power spectra.

The power spectrum of the resonator is given by

\[
S_4(\omega) = \frac{\kappa}{2\pi} \int_{-\infty}^{\infty} \langle \hat{a}^\dagger(\tau) \hat{a}(0) \rangle e^{-i\omega \tau} d\tau
\]

\[
= \frac{\kappa}{2\pi} \text{Re} \left\{ \int_{0}^{\infty} \langle \hat{a}^\dagger(\tau) \hat{a}(0) \rangle e^{-i\omega \tau} d\tau \right\},
\]

where the first order correlation function can be written as

\[
\langle \hat{a}^\dagger(\tau) \hat{a}(0) \rangle = \text{Tr} \left\{ \hat{a}^\dagger \left( U(\tau) \hat{a} \rho_{ss} U^\dagger(\tau) \right) \right\},
\]

for the time-evolution operator \( U(t) = e^{\mathcal{L} t} \). We can measure the total emitted power by integrating the power spectrum

\[
\int_{-\infty}^{\infty} S_4(\omega) d\omega = \kappa \int_{0}^{\infty} \langle \hat{a}^\dagger(\tau) \hat{a}(0) \rangle \delta(\tau) d\tau = \kappa \langle \hat{a}^\dagger \hat{a} \rangle_{\rho_{ss}} = \kappa \langle N_r \rangle_{\rho_{ss}},
\]

which is equivalent to the calculated resonator current. This equation shows that the transport properties of the circuit, the area of the power spectrum, depend on the non-oscillatory steady state density matrix \( \rho_{ss} \) which is the kernel of the Lindblad master equation

\[
\dot{\rho}_{ss} = \mathcal{L}[\rho_{ss}] = 0.
\]

On the other hand, the shape of the spectrum is defined by the damped oscillatory eigenspace of the Lindblad operator that is orthogonal to \( \rho_{ss} \).
In addition to the resonator spectrum above, we will investigate in the following section the bright state spectrum, as measured at port 2

\[ S_2(\omega) \approx \frac{\gamma_b}{2\pi} \int_{-\infty}^{\infty} \langle \hat{\sigma}_b^\dagger(\tau)\hat{\sigma}_b(0) \rangle e^{-i\omega \tau} \, d\tau, \]

(6.29)

\[ (6.30) \]

Here, \( S_2 \) is only an approximate spectrum as it uses the first order correlation function in \( \sigma_b \), while we know from the current \( j_b, \gamma_b \) that this actual process is of higher order. This approximation is applicable in the weak driving limit, where the doubly excited state is not occupied, which is the case in the experiments.

## 6.4 Results

We will present experimental results for four different cases which we will compare against each other to gain insight into noise assisted transport (NAT). The qubits will be exposed to two different noise PSDs, either strongly Markovian white noise, or a non-Markovian Lorentzian noise that has its peak centred at the bright-dark energy gap (see Fig. 6.2c). We study the transport under coherent driving which creates conditions similar to typical laser spectroscopy, and under incoherent driving which is meant to resemble natural illumination conditions.

### 6.4.1 Coherent drive and white noise

In Fig. 6.3a we present the emission spectra of the bright state measured at port 2 (purple) and of the resonator at port 4 (orange) in the case of coherent driving and white Gaussian noise. The coherent drive has frequency \( \omega_b \) and an amplitude corresponding to a bright state Rabi frequency of \( \Omega_R/2\pi = 14 \text{ MHz} \). The Markovian noise has a bandwidth of 325 MHz and adjustable amplitude. Its noise strength is characterised by the integrated flux noise power \( \Phi_W^2 \). Without any noise applied, there is no power output from the resonator which confirms that there is no transport from bright \( |b\rangle \) to \( Q_3 \) due to strong off-resonance and that there is no bright to dark transport since these states are decoupled. At weak noise power \( \Phi_W^2 \), the resonator spectrum shows a double peak at the frequencies of \( |d_1\rangle \) and \( |d_2\rangle \), while the bright spectrum decreases in magnitude. This indicates a bright to dark transport due to the dephasing noise. As \( \Phi_W^2 \) is increased, the bright state spectrum decreases and widens while the resonator
Fig. 6.3 (a,d) Experimentally measured PSDs and (b) PSD obtained from master equation calculations as a function of noise power $\Phi_2^2$, displaced by 0.2 Photons s$^{-1}$ Hz$^{-1}$. (c,f) Integrated PSDs and harvest efficiency $\eta$ as obtained from experiments (symbols) and from simulations (lines). Spectra were obtained under white noise (top) and under Lorentzian noise (bottom) with centre frequency $\nu_L = 190$ MHz. (e) The resonator output power under weak Lorentzian noise for different centre frequencies shows 2 resonance peaks which agree with the energy difference between $|b\rangle$ and the two hybrids $|d1\rangle$ and $|d2\rangle$. Figure used with permission of A. Potočnik.
power output increases up to $\Phi_2^b = 0.89\,\text{pWb}^2$ and decreases subsequently. Since the broadening of $|b\rangle$ is due to the noise induced dephasing, we can determine the pure dephasing rate of the bright state $\gamma_b^b$. In addition, we observe a collapse of the distinct $|d_1\rangle$ and $|d_2\rangle$ peaks into a single peak at the frequency of $|d\rangle$ for noise powers above $\approx 2\,\text{pWb}^2$, indicating a changeover from a strong coupling regime ($2J_{d3} \gtrsim \gamma_b^b$) to the weak coupling regime ($2J_{d3} \lesssim \gamma_b^b$). We note, that the current from $|d\rangle$ to $|q3\rangle$ is still coherent in its nature, since it is only mediated by a coherent coupling $J_{d3}$ in the Hamiltonian (see Eq. 6.19), even under strong noise.

The simulated spectra in Fig. 6.3b show excellent agreement between model and experiment, in shape and magnitude, which confirms that the superconducting circuit is suitable for this type of study and that its design meets our initially set out criteria. It has to be pointed out that this case of coherent drive and white noise lies within the approximations of the Lindblad master equation such that we can trust the simulations to be accurate. The total power output in Fig. 6.3c, as obtained by integrating the PSDs, shows a rapid initial drop of the bright state emission $P_2$ together with a corresponding increase in resonator emission $P_4$, as a result of noise-induced incoherent transitions between $|b\rangle$ and $|d\rangle$ [31, 44]. This results in an increase in transfer efficiency

$$\eta = \frac{P_4}{P_4 + 2P_2}, \quad (6.31)$$

where the factor 2 takes into account that $P_2$ measures only the bright state emission into one direction, while the fluorescence happens bidirectional. After reaching the highest extracted power and efficiency, both, $P_2$ and $P_4$, drop for further increasing noise, indicating that the total absorption of our light-harvesting system decreases. Maximum efficiency is achieved where the bright to dark transport rate equals the dark to trap transport rate, so at the strong-to-weak coupling crossover $2J_{d3} \approx \gamma_b^b$.

### 6.4.2 Coherent drive and Lorentzian noise

It has been conjectured that structured environmental noise, as caused by damped vibrational modes of the protein scaffold of light-harvesting complexes, could give enhanced energy transfer efficiencies compared to white noise [28, 57]. To demonstrate this concept, we narrowed the dephasing noise to a Lorentzian spectrum with centre frequency $\nu_L = 190\,\text{MHz}$ and width of $\Delta\nu_L = 10\,\text{MHz}$, which corresponds to the environmental noise expected from vibrational modes in light-harvesting complexes. Since the bandwidth of the Lorentzian is comparable to the decay rates $\gamma_b, \gamma_{\text{pur}}$, the
6.4 Results

Fig. 6.4 Integrated powers for white noise (crosses) and Lorentzian noise (dots) against total noise power $\Phi^2_W$ and $\Phi^2_L$. Very strong noise effectively decouples $Q_2$ from the driving which reduces absorption into the bright state.

The spectra obtained for Lorentzian noise (Fig. 6.3d) are very similar to the ones obtained under white noise (Fig. 6.3a) with a few distinct differences. The double peak in the resonator output is more asymmetric and centred on $\nu_{d1}$, since the Lorentzian is tuned to the $|b\rangle - |d_1\rangle$ energy gap $\nu_L = \nu_b - \nu_{d1}$. The integrated power $P_4$ peaks with almost twice the maximum power transferred under white noise, before displaying very similar decreasing characteristics as expected for NAT. This leads to an increased maximal efficiency of $\eta_L^{max} = 58\%$ without changing the drive amplitude or any decay rates.

When sweeping $\nu_L$ for weak noise power $\Phi^2_L = 0.016 \text{ pWb}^2$ it is possible to resolve two peaks in the integrated power output at the resonator $P_4(\nu_L)$ (Fig. 6.3e), corresponding to resonances with $|b\rangle$ to $|d_1\rangle$ and $|d_2\rangle$ energy differences, while almost no energy is transported when the Lorentzian is off-resonant with these transitions. This exhibits that the NAT is not caused by any arbitrary noise, but especially the narrow parts of the noise PSD which are resonant with energy gaps of the system.

In particular, we can relate the rise in harvested power $P_4$ and the drop-off of $P_2$ and $P_4$ for stronger noise to noise power amplitude and total noise power. By displaying the integrated powers for white (crosses) and Lorentzian (dots) total noise powers on top of each other (Fig. 6.4), we can immediately see that the total absorbed power $P_{tot} = 2P_2 + P_4$ decreases with very similar slopes for both environments,
Fig. 6.5 Integrated powers for white noise (crosses) and Lorentzian noise (dots) against noise PSDs $S_W$ and $S_L$ at energy gaps $\Delta_{b,d_1}$ and $\Delta_{b,d_2}$.}

despite the very different transport characteristics. Since the total noise powers $\Phi^2_W, \Phi^2_L$ correspond to the integrated noise PSDs, they take into account the noise strengths at any frequency. This suggests that the decrease in absorption is insensitive to the noise frequency and instead depends on the pure dephasing. In the context of the quantum Zeno effect [40, 99] we can understand the suppression of absorption as an effective decoupling from the transmission line due to strong interaction between $Q_2$ and the noise ($\Omega_R < \gamma_b^h$).

With the noise PSDs we can work out the sum of the noise powers at the relevant energy gaps $\Delta_{b,d_1}$ and $\Delta_{b,d_2}$ as being approximately $S_W = 2 \Phi^2_W/325\text{MHz}$ and $S_L = \Phi^2_L/15.5\text{MHz}$ at $\nu_L = \Delta_{b,d_1}$, where the power at $\Delta_{b,d_2}$ is negligible. These estimates can quantify the amount of noise that contributes towards energy transfer. In Fig. 6.5 we compare the integrated powers under white (crosses) and Lorentzian noise (dots) for similar noise powers. Most prominently we can observe very similar increases in total harvested power $P_4$ for both noise types, where the white noise $P_4$ drops off earlier due to the earlier onset of the quantum Zeno effect. This confirms the previous observation that only the part of the noise PSD contributes to NAT that is resonant with energy gaps of the system.

Thus, the main difference between the white noise and the Lorentzian noise can be characterised by the ratio between “useful” noise that causes bright to dark energy transport, and the total noise power which leads to a decrease in absorption that should be avoided in any light-harvesting complexes.
6.4 Results

6.4.3 Coherent drive, coherent noise

To prove the above insights, we further narrowed the Lorentzian down to a coherent tone which concentrates all noise at $\nu_L = \Delta_{bd1}$. As expected, the transport efficiency reaches almost 100% (see Fig. 6.6c) already for very low noise powers $\Phi^2_c$. Similar to the other noise types, the absorption decreases as the noise is increased, although it happens at a different order of magnitude of noise power. The strong depletion of $|b\rangle$ is a result of a coherent population trapping in $|d_1\rangle$. This phenomenon is known in literature as electromagnetically induced transparency (EIT) [2, 91] of the bright state. Although not relevant for actual light-harvesting complexes, this example demonstrates how NAT can be significantly enhanced by focusing the environmental noise around energy gaps and engineering it as thin as possible to avoid any loss of absorption. On the other side it might be advantageous to design the electronic system such that energy gaps match already existing environmental peaks to harness them optimally.

6.4.4 Incoherent excitation

In the light-harvesting community is a long standing debate about the possible differences in the dynamics between natural light-harvesting under incoherent solar illumination and the photoreactions measured under coherent laser excitation, as used to perform any kind of fast transient spectroscopy, such as transient absorption or 2D electronic spectroscopy. While there are a number of steady-state spectroscopic techniques that work with incoherent light, such as linear absorption, there are no incoherent pulsed transient techniques that can reveal dynamical properties.

It is definitely relevant to know to what extent observations made under coherent illumination can be used to predict behaviour under sunlight. There are several good arguments on both sides either suggesting fundamental or negligible differences. Although we will not go too much into detail here, we take this as a motivation to
Fig. 6.7 NAT under incoherent illumination. (a,d) Experimentally measured PSDs and (b) PSD obtained from master equation calculations as a function of noise power $\Phi^2$, displaced by 0.2 Photons s$^{-1}$ Hz$^{-1}$. (c,f) Integrated PSDs and harvest efficiency $\eta$ as obtained from experiments (symbols) and from simulations (lines). Spectra were obtained under white noise (top) and under Lorentzian noise (bottom) with centre frequency $\nu_L = 190$ MHz. (e) The resonator output power under weak Lorentzian noise for different centre frequencies shows only a broad resonance. Figure used with permission of A. Potočnik.
measure steady-state properties of our artificial light-harvesting circuit under incoherent illumination. While this is not revolutionary yet, additional gating could be used in future experiments to enable pulsed incoherent illumination.

In Fig. 6.7 we present the spectra as obtained for illumination with an incoherent microwave signal with a flat PSD spanning frequencies $5.9 - 6.9$ GHz. Since it is not possible to distinguish between re-emitted photons and transmitted photons at port 2, we perform a background subtraction with the incoherent signal, such that the difference $S_2 - S_{In}$ is a combination of absorption and emission spectrum. In the absence of any noise we can observe emission from the resonator which indicates a population of the dark state from the incoherent driving. As the white noise (Fig. 6.7a) or the Lorentzian noise (Fig. 6.7d) is increased, the harvested power increases up to a maximum value and decreases for larger noise powers, while the background subtracted power at port 2 decreases monotonically. Also we can observe that the Lorentzian noise leads to an increased harvested power compared to the white noise, confirming our observations of the previous section.

A major difference to the coherently driven cases is that the total absorbed power does not decrease as fast as for larger noise powers. We can explain this behaviour by comparing the spectral overlap between the driving spectrum and the bright state spectrum. As the noise is increased, the bright state broadens and lowers which leads to a rapidly decreased overlap with the spectrum of the coherent drive, while the overlap with the incoherent broad band drive is almost unchanged. With a weaker suppression of absorption, the harvested power is not decreased as strongly as under the narrow band coherent drive. Yet, the quantum Zeno effect is observable as a weak decrease in harvested power and as a peak shift in the bright spectrum from the bright state frequency down to the unperturbed $Q_1$ frequency, as $Q_2$ becomes increasingly decoupled from the drive, $Q_1$, and $Q_3$. Since the coupling $J_{12}$ is an order of magnitude larger than the Rabi frequency and $J_{23}$, this decoupling and peak shift happens only for very strong noise.

The direct excitation of the dark state can be interpreted as dephasing induced by the incoherent illumination, which decreases the $Q_1$-$Q_2$ coherence and therefore incoherently populates the dark state. While the incoherent excitation is weak enough, this dephasing does not affect the coherences between the dark state and $Q_3$, such that their coherent superpositions $|d_1\rangle$ and $|d_2\rangle$ are still observable.
6.5 Conclusions

Superconducting circuits offer an optimal playground to study environmental effects on light-harvesting processes. Due to the well explored design and sample preparation process, it is possible to manufacture circuits as experimental models at unprecedented precision, from the weak to strong coupling regime. We were able to demonstrate that it is possible to study noise assisted transport in these superconducting circuits, by performing spectroscopy on a single system, avoiding ensemble averages. With the possibility to study the effects of almost arbitrary classical noise and drive power spectral densities, we could show that NAT is most efficient if the noise PSD is concentrated at the energy gaps across which transport is desired, while any excess noise only leads to a reduction in transport due to an effective decoupling. We could show that a spectrally broad incoherent illumination can protect transport across a wider range of noise powers compared to the narrow band coherent excitation, while exhibiting similar increased harvest powers for Lorentzian noise.

This approach can be extended to perform time-resolved experiments and 2D spectroscopy. It is possible to implement larger chromophore networks and even quantum environments, by means of quantum harmonic oscillators.
Chapter 7

Conclusions and Prospects

This work presents major developments in the field of matrix product states (MPS) that enable the simulation of realistic molecular exciton phonon dynamics towards the simulation of natural and artificial light-harvesting complexes. We demonstrated the capabilities of the resulting tree tensor network states (TTNS) algorithm by studying vibronic singlet fission (SF) dynamics to a detail that revealed reaction mechanisms and pathways. As a viable experimental model, we also demonstrated how superconducting circuits can be used to precisely model light-harvesting processes with unprecedented control over both, system and environmental parameters.

In particular, we developed a clustering and entanglement renormalisation scheme that enables an almost automated interfacing of TTNS with \textit{ab initio} electronic structure calculations, to simulate dynamics of complex and realistic vibronic Hamiltonian models. We presented detailed environmental observables and developed a novel approach to visualising the energy surfaces that underlie the simulated SF dynamics. By combining these insights we could identify the real-time contribution and the role of each individual environment to unravel the mechanism of SF in DP-Mes. We demonstrated that purely CT-mediated SF in DP-Mes can be rapid despite the 680 meV energy barrier, as vibronic super-exchange creates an effective coupling between singlet and triplet pair states. This new technique is able to reveal non-Born-Oppenheimer dynamics by simultaneously tracking the electronic wave function on surfaces created by multiple entangled environmental states, which could have important applications in a wide range of optoelectronic systems. The unique capabilities of TTNS led to collaborations with the Nanophotonics group at Universidad Autonoma de Madrid, in particular Carlos and Javier, applying our technique to the sub-Ohmic SBM and to large polaritonic systems. To the best of our knowledge, it is the only technique that can simulate the
multi-dimensional polaritonic problem of the interaction between $> 10$ coupled organic molecules inside a cavity, each connected to its own, arbitrary phonon environment, at reasonable efficiency.

As an alternative to molecular light-harvesting model systems which are very difficult to precisely tune and control, we presented a realisation of a minimal light-harvesting system in a superconducting circuit. We demonstrated the flexibility and control provided by the circuits and could confirm that noise assisted transport is optimal under narrow, peaked spectral densities.

7.1 Prospects

There are a number of technical advancements that can be made in TTNS based on the presented techniques:

- The bosonic shift, here only defined for a variational ground state optimisation, can be also performed in a time-dependent form, by measuring the displacement of a boson and applying a unitary transformation to the Hamiltonian and TTNS simultaneously. This would reduce the computational effort for strongly displaced modes, as they could appear in photo-isomerisation processes.

- A compression of matrix product operators (MPO) that performs an SVD to separate local Hilbert space and bond space can be used to reduce the order of MPO tensors and make them computationally feasible for bosonic chains with large Hilbert space.

- The visualisation of energy surfaces is very complex due to the large number of surfaces. An algorithm that can identify surfaces and hide them according to their relevance for the dynamics could reduce the complexity and improve accessibility for a wider readership.

Synergies between TTNS and thermofield approach

Finite temperature simulations can be improved by adopting the thermofield approach [33]. While imaginary time-evolution suffers substantial computational effort due to large bond dimensions together with issues arising from truncating the environmental chain, the thermofield approach offers the advantage of a precise initialisation into a thermal state at the cost of an additional environment. Since the ER-network of the
TTNS allows a straightforward implementation of multiple environments, this could be a feasible option to study finite temperature vibronic dynamics, and temperature activated processes. It would also be interesting to study the dynamic entanglement properties between the two chains representing the single thermal environment as this determines also the efficiency of the ER-network.

**End-of-chain time-evolution via machine learning**

Simulating long-time dynamics with short and highly truncated semi-infinite chains is a highly desirable, yet hard problem since it would need a special kind of open boundary condition that optimally allows the dissipation of energy without creating artificial reflections. Training a TTM to perform an end-of-chain evolution only yielded a 50% reduction of reflections due to the intermediate coupling regime of the uniform chain. Since along the uniform chain all dynamics should be highly predictable, it should be possible to train a neural network to perform the end-of-chain time-evolution, based on the effective Hamiltonian and the state of the last bosonic site. To avoid the need to store the state history for non-Markovian effects, it might be necessary to let the neural network predict the new right effective Hamiltonian, after the last bosonic site has been time-evolved. This evolution of the effective Hamiltonian could be straightforwardly integrated into the TDVP scheme and lead to significant reductions in computational complexity.

**Classical environments and mixed state representations**

For the simulation of weakly coupled classical environments it is possible to apply Lindblad collapse operators to the MPS. Especially for extended systems, the inefficient representation of the density matrix in terms of an MPO could be avoided by allowing an open bond in the direction of the classical environment which effectively captures the mixing induced by that environment.

**Closing the gap to ML-MCTDH**

In this work, we developed MPS in a direction which is very close to ML-MCTDH, while taking advantage of its roots in condensed matter theory and insights about entanglement structure to significantly reduce computational effort. It would be interesting to proceed even further and apply the presented technique to real-space Hamiltonians with the possibility to move towards quantum chemistry applications.
Equivalently, introducing the presented techniques in ML-MCTDH, which is already more mature and well established, could yield significant improvements and accelerate materials discovery.

Interesting applications

It would be interesting to simulate finite temperature dynamics of DP-Mes for possible temperature dependence and compare with experimental data. Applying TTM to DP-Mes could be interesting to assess the applicability of TTM to capture the dynamics of multi-environment models.

While this work explored avoided crossing dynamics, it would be very interesting to apply TTNS to molecules known to exhibit conical intersection dynamics.

Finally, the original objective to simulate exciton transport in larger photosynthetic light-harvesting complexes such as the Fenna–Matthews–Olson complex (FMO) [105] or LH2 rings should be possible with the advancements made.
List of publications

1. Simulating open quantum dynamics with time-dependent variational matrix product states: Towards microscopic correlation of environment dynamics and reduced system evolution,
   **Florian A. Y. N. Schröder** and Alex W. Chin,
   Physical Review B 93, 075105 (2016),
   see Chapter 4

2. Multi-dimensional Tensor Network Simulation of Open Quantum Dynamics in Singlet Fission,
   **Florian A. Y. N. Schröder**, David H. P. Turban, Andrew J. Musser, Nicholas D. M. Hine, and Alex W. Chin,
   currently in submission, preprint at arXiv:1701.01362,
   see Chapter 5

3. Studying light-harvesting models with superconducting circuits,
   Anton Potočnik, Arno Bargerbos, **Florian A. Y. N. Schröder**, Saeed A. Khan, Michele C. Collodo, Simone Gasparinetti, Yves Salathé, Celestino Creatore, Christopher Eichler, Hakan E. Türeci, Alex W. Chin, and Andreas Wallraff,
   Nature Communications 9, 904 (2018)
   see Chapter 6

4. Uncovering nonperturbative dynamics of the biased sub-Ohmic spin-boson model with variational matrix product states,
   Carlos Gonzalez-Ballestero, **Florian A. Y. N. Schröder**, and Alex W. Chin,

5. Tensor network simulation of non-Markovian dynamics in organic polaritons,
   Javier del Pino, **Florian A. Y. N. Schröder**, Alex W. Chin, Johannes Feist,
and Francisco J. Garcia-Vidal,

*currently in submission*, preprint at arXiv:1804.04511
References


References


References


1723. doi: 10.1038/ncomms6156. URL http://www.nature.com/doifinder/10.1038/ncomms6156.


References


10.1038/nchem.1801. URL http://www.nature.com/doifinder/10.1038/nchem.1801.


