Quantum Stochastic Walks
A model for coherent and incoherent transport on networks

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### List of symbols and abbreviations

<table>
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<th>Description</th>
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<tbody>
<tr>
<td>CTRW</td>
<td>Continuous-time random walk</td>
</tr>
<tr>
<td>CTQW</td>
<td>Continuous-time quantum walk</td>
</tr>
<tr>
<td>QSW</td>
<td>Quantum stochastic walk</td>
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<tr>
<td>EST</td>
<td>Expected survival time</td>
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<tr>
<td>TDM</td>
<td>Transition dipole moment</td>
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<td>FMO</td>
<td>Fenna-Matthews-Olsen complex</td>
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<tr>
<td>PIMC</td>
<td>Path Integral Monte Carlo</td>
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<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
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<tr>
<td>BChl</td>
<td>Bacteriochlorophyll</td>
</tr>
<tr>
<td>$\mathbf{A}$</td>
<td>Matrix representation of a linear operator $A$</td>
</tr>
<tr>
<td>$\rho_S(t)$</td>
<td>Reduced density matrix</td>
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<td>$\rho_\alpha(t)$</td>
<td>Reduced density matrix for the QSW with interpolation parameter $\alpha$</td>
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<td>$P_k(t)$</td>
<td>Population of the state $</td>
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<td>$C_{km}(t)$</td>
<td>Coherence between the states $</td>
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<td>$\eta(\alpha)$</td>
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Introduction

In this thesis I will focus on studying both quantum mechanical and classical dynamical processes on various networks. These networks can represent, for instance, regular $d$-dimensional lattices found in solid state physics [1] or more complex irregular networks such as polymers and hyperbranched molecular structures [2]. Ultra-cold Rydberg gases also provide an interesting example of a weighted network, where the weights (interactions) depend on the distances between the Rydberg atoms and the nodes are given by the effective two-level systems of electronic Rydberg states that are relevant for excitation energy transfer [3, 4]. For each of these examples it holds that their respective transport properties strongly depend on the specific topology of the network. For instance, in regular periodic lattices one encounters Bloch oscillations [1], while in disordered systems one can encounter Anderson localization [5]. Another example is in polymer dynamics, where the connectivity properties of the polymer determine its relaxational properties [6].

Classical transfer processes on networks can be successfully described by the continuous-time random walk (CTRW), which is a generalization of the well known (discrete-time) random walk [7]. This model has been applied to various physical systems, such as percolation [8] and energy transfer in molecular complexes [9]. For example for the latter, this is done by modeling the dynamics of the Frenkel exciton at high temperatures by a classical master equation [9]. Analogous to the CTRW, one can also study continuous-time quantum walks (CTQW) [10, 11]. These are constructed by taking the classical transfer matrix as the Hamiltonian of the system. The resulting Schrödinger equation can be directly related to the well known tight binding model of solid state physics, but with a general network instead of a periodic lattice [11].

In this thesis, I will study a model for transfer processes on networks that combines both the CTRW and the CTQW as limiting cases. This model is known as the quantum stochastic walk (QSW), but has received
little attention up till now \([12, 13, 14, 15, 16]\). It is based on the Lindblad master equation that describes the dynamics of an excitation in a system that is embedded in a large environment. While the normal evolution of the excitation is described by the Hamiltonian of the CTQW, the incoherent classical dynamics is assumed to be generated by the interactions with the environment. This feature is already present in many other master equation approaches, such as the well established Redfield theory \([17, 18]\). The major difference is, however, that in these approaches the incoherent dynamics occurs between the eigenstates of the system, while for the QSW it occurs between the nodes of the network \([12]\). This makes this model an interesting alternative to explore a different type of dynamics that can be generated by interactions with an environment. It can also provide further insight into the differences between classical and quantum dynamics and, most importantly, the intermediate regime. The goal of this thesis is to work out the mathematical details of this model and to apply it to various types of networks and configurations in order to establish its usefulness and validity in modeling transport processes in complex systems.

This thesis is structured as follows:

- Part I of this thesis deals with the theoretical background of the QSW. In chapter 1, I will introduce the mathematical definition of a network and I will first review the definitions of both the CTRW and the CTQW. The latter will be motivated by shortly discussing the article in which this model first appeared. Then I will turn my attention to the (reduced) dynamics of excitations in an open quantum system and I will review the concept of quantum Markov processes, leading to the definition of the Lindblad master equation. I then use this Lindblad equation to define the QSW and its associated master equation. Finally, I will focus on how the QSW allows me to model the transitions between the CTRW and the CTQW.

- In chapter 2, I will describe transport processes in the context of the QSW. In particular, I will demonstrate how to model and attach sources and drains to a network. I will also describe the relation of modeling drains and absorption processes in the QSW formalism to both the CTRW and the CTQW. Finally, I will introduce the concept of the expected survival time (EST) as a measure for (in)-efficiency of transport through the network.
In part II of this thesis I will apply the theoretical formalism that was introduced before to various networks and physical systems. In chapter 3, I will mainly discuss various examples of networks that are attached to a source and a drain and will focus on describing the behaviour of the EST for all of them. In particular, I will consider a monomer, a dimer, topologically disordered networks and a lambda-level system. For the last example, I will discuss how different initializations of the system can lead to a big increase in the transport efficiency. For the topologically disordered networks I will explain how its transport efficiency can be understood by mapping the network to a disordered dimer.

In chapter 4, I will describe the behaviour of the von Neumann entropy for the QSW. After first reviewing the scaling exponents related to the classical Shannon entropy of a CTRW, I will generalize these exponents to the QSW. Namely, I will show, for both a Sierpinski gasket and a linear chain, that the von Neumann entropy exhibits a logarithmic growth regime for a large range of couplings to the environment. This growth rate can, in turn, be related to the information dimension associated to the QSW and, in the classical limit, to the spectral dimension of the CTRW.

In the last chapter of this thesis, chapter 5, I will apply the QSW to describe excitation energy transfer on the FMO complex. This is done by using the microscopic parameters that were obtained by large scale Molecular Dynamics (MD) simulations of this complex. To verify my predictions, I compare them to the results obtained from Path Integral Monte Carlo (PIMC) simulations. Finally, I also compute the linear absorption spectrum and compare it to an experimental result and to the one obtained by semi-classical wavepacket dynamics.

During the process of writing this thesis, I have published several articles related to various chapters and sections in this thesis. In particular, in Ref. [19], I discussed the implementation of sources and drains into the QSW and applied it to topologically disordered networks. Here in this thesis, the former is described in more detail in chapters 1 and 2 and the latter is discussed in sections 3.2 and 3.3. During the work on that topic, I had many fruitful discussions with J. Kohlberger about the underlying theoretical model, although he applied it to different networks in his diploma thesis. The contents of Ref. [20] are worked out in detail in section 3.4.
An article related to the contents of Chap. 5 has been placed on the arXiv preprint server [21], but has not been published in a refereed journal. During the work on this chapter, L. Mühlbacher has provided the Path Integral Monte Carlo simulation data, also appearing in Ref. [22], to which I compared my theoretical model. He has also participated in many discussions about my numerical results.

Finally, the contents of Chap. 4 represent my latest work and have not yet been submitted to a refereed journal. In all my (published) work, O. Mülken and Prof. dr. A. Blumen have provided supervision and guidance.
Part I

Part 1: Theoretical framework
Chapter 1

Quantum Stochastic Walks

1.1 Continuous-time quantum and random walks on networks

1.1.1 Networks

In the mathematical literature, a network is defined by the concept of a graph. Formally, a graph $G$ is a pair $G = (V, E)$, where $V$ is the set of nodes and $E$ is the set of edges between the nodes [23]. Here I restrict myself to the situation of undirected edges and do not allow for multiple edges between a set of nodes, i.e. I only consider simple graphs. Graphs can be characterized in many different forms, but one form is specifically suited to the applications appearing in this thesis, namely the connectivity matrix $A$. It is defined as follows [23]:

$$A_{kl} = \begin{cases} 
d_j & \text{for } k = j \\
-1 & \text{if nodes } k \text{ and } j \text{ are connected} \\
0 & \text{else} 
\end{cases} \quad (1.1)$$

The connectivity matrix is also often referred to as the graph Laplacian $L$. It has the following important properties [23]: (a) $A$ is a symmetric matrix (b) all eigenvalues $\lambda_n$ of $A$ are positive, i.e. $\lambda_n \geq 0$, and (c) $A$ always has at least 1 eigenvalue equal to 0. Its degeneracy reflects the number of disjoint components in the network.

In this representation of the connectivity matrix, each node $k$ of the network is represented as a basis vector $\bar{e}_k$ in an $N$-dimensional vector space. For later use it is convenient to write these basis vectors in Dirac notation,
\[ \bar{c}_k \equiv |k\rangle. \] They form a complete set of states and satisfy the completeness relation \( \sum_k |k\rangle \langle k| = \mathbb{I} \).

### 1.1.2 Continuous-time random walks

In physical systems related to networks, one is mostly interested in stochastic processes occurring on them. An important class of stochastic processes are Markovian processes. In this section, the discussion of these processes closely follows the contents of Ref. [7].

For Markovian processes, the conditional probability density at a time \( t_n \), given the value \( y_{n-1} \) at \( t_{n-1} \), is uniquely determined and not influenced by the values at earlier times. More formally, this condition can be written as:

\[
P_{1|1}(y_{n-1};t_{n-1}|y_{1};t_{1};\ldots;y_{n-1};t_{n-1}) = P_{1|1}(y_{n},t_{n}|y_{n-1},t_{n-1}),
\]

for \( t_1 < t_2 < \ldots < t_n \), where in general these conditional probabilities are defined as:

\[
P_{l|k}(y_{k+1},t_{k+1};\ldots;y_{k+l}|y_{k},t_{k}) = \frac{P_{l+k}(y_{1},t_{1};\ldots;y_{k},t_{k};y_{k+1},t_{k+1};\ldots;y_{k+l},t_{k+l})}{P_{k}(y_{1};t_{1};\ldots;y_{k},t_{k})}.
\]

\( P_{1|1} \) is also called the transition probability. Markov processes can alternatively be characterized by both the Chapman-Kolmogorov equation

\[
P_{1|1}(y_{3},t_{3}|y_{1},t_{1}) = \int dy_{2}P_{1|1}(y_{3},t_{3}|y_{2},t_{2})P_{1|1}(y_{2},t_{2}|y_{1},t_{1}),
\]

and

\[
P_{1}(y_{2},t_{2}) = \int dy_{1}P_{1|1}(y_{2},t_{2}|y_{1},t_{1})P_{1}(y_{1},t_{1}).
\]

These two conditions ensure that the entire Markov process can be constructed from \( P_{1} \) and \( P_{1|1} \). Conceptually, the Chapman-Kolmogorov equation states that the transition probability from going from \( y_{1} \) to \( y_{3} \) is obtained by considering an intermediate point \( y_{2} \) and summing over all its possible positions. Note that this is also similar to the path integral formulation of quantum mechanics [24].

For a homogeneous Markov process, where the transition probabilities \( P_{1|1}(y_{2},t_{2}|y_{1},t_{1}) \) only depend on the time difference \( \tau = t_{2} - t_{1} \), the Chapman-Kolmogorov equation can also be written in the following integro-differential form:

\[
\frac{\partial P(y,t)}{\partial t} = \int dy' [W(y|y')P(y',t) - W(y'|y)P(y,t)].
\]
Here $W(y|y')$ is the transition probability per unit time. Note that Eq. (1.6) is an equation for the transition probability, given some initial condition, and not for the probability distribution of the stochastic process. This form of the Chapman-Kolmogorov equation is called the master equation. When the state space $Y$ is discrete ($Y = \{y_n\}$), it takes the following form:

$$\frac{dp_n(t)}{dt} = \sum_{n'} [W_{nn'}p_{n'}(t) - W_{n'n}p_n(t)].$$

(1.7)

The first term on the r.h.s. represents the gain due to transitions from a state $n'$, while the second term represents a loss term. This discrete form of the master equation is the most relevant for this thesis, since a network constitutes a discrete set of states. The master equation is also more convenient than the Chapman-Kolmogorov equation since in many physical situations one can estimate the transition rates $W_{nn'}$ directly.

Now consider the matrix $T$ defined by $T_{nn'} = W_{nn'}$ and $T_{nn} = -\sum_{n'} W_{nn'}$. This allows the master equation to be written as:

$$\frac{d\tilde{p}(t)}{dt} = T\tilde{p}(t),$$

(1.8)

where $\tilde{p}$ is a vector with components $p_n(t)$ and whose solution is given by $\tilde{p}(t) = \exp(Tt)\tilde{p}(0)$. The equation above is the defining equation for a continuous-time random walk (CTRW) on a network. When all the nonvanishing transition rates are equal to $\gamma$, the transfer matrix $T$ can be related to the connectivity matrix $A$ by $T = -\gamma A$. In this case the time evolution for the CTRW can be written as:

$$\tilde{p}(t) = \exp(-\gamma At)\tilde{p}(0).$$

(1.9)

The positivity of the eigenvalues of $A$ ensures that there is a stationary solution $\tilde{p}^*$ of the master equation, corresponding to the eigenvector of $A$ with eigenvalue 0:

$$\tilde{p}^* = \frac{1}{N} \sum_n |n\rangle.$$

(1.10)

### 1.1.3 Continuous-time quantum walks

**The exact cover problem**

Continuous-time quantum walks (CTQW) were first introduced by Farhi and Gutmann [10]. Before giving the general definitions, I use the problem that
they considered as an introductory example: given a \( m \) by \( n \) matrix \( B \) over \( \mathbb{Z}_2 \), with \( m \leq n \), does there exist a solution to the set of equations

\[
\sum_{k=1}^{n} B_{jk} x_k = 1 \quad \text{for } j = 1, \ldots, m,
\]

with the \( x_k \in \mathbb{Z}_2 \)? This problem is also referred to as the exact cover problem. A brute-force approach to solve this problem is not efficient. The standard way to solve it is to transform the set of equations into a decision tree \( T \) under the influence of certain constraints. This tree is constructed as follows: at the top, \( T \) consists of 1 node that is connected to two other nodes on the level below, corresponding to the two different choices for \( x_1 \). Both of these two nodes are also connected to two nodes respectively, leading to four nodes in the second level, corresponding to the 4 possible solutions for \((x_1, x_2)\). Continuing this process leads to a tree with \( 2^n \) nodes in the \( n \)-th level. An illustration of \( T \) is given in Fig. (1.1).

Because of the specific form of Eq. (1.11), not all branches of \( T \) have to be considered. Consider for example an index \( j \) such that \( B_{j1} = B_{j2} = 1 \). In this case, the starting combination \((x_1, x_2) = (1, 1)\) does not lead to a valid solution and all combinations of the form \((1, 1, x_3, \ldots, x_n)\) do not have to be considered anymore. More general, if for a sequence \((x_1, \ldots, x_l)\) it holds that \( \sum_{k=1}^{l} B_{jk} x_k \geq 2 \), then all sequences of the form \((x_1, \ldots, x_l, x_{l+1}, \ldots, x_n)\) do not have to be considered. These branches are then deleted from \( T \). Note that the exact-cover problem only has a solution when there is at least 1 node at level \( n \).
The exact cover problem can now be solved by considering a random walker on the decision tree $T$ with the constraints described above. If the random walker reaches a node at the $n$-th level a valid solution is found. This process can be described by a CTRW on $T$. Without loss of generality, we can assume that the transition rates are given by $\gamma = 1$, since other values merely lead to a rescaling of time. The transfer matrix $T$ is thus given by $T = -\gamma A_T = -A_T$, where $A_T$ is the connectivity matrix corresponding to $T$. The master equation for the CTRW (see Eq. (1.8)) is then given by:

$$\frac{d\tilde{p}(t)}{dt} = -A_T\tilde{p}(t), \quad \tilde{p}(0) = |0\rangle,$$

(1.12)

where $|0\rangle$ is the node of $T$ in level 0. Depending on the specific structure of $T$ it can happen that reaching the $n$-th level is not achievable in polynomial time.

**Formulation of the CTQW**

The question Farhi and Gutmann now asked themselves was if a quantum mechanical time evolution on $T$ could speed up this process [10]. They proposed that one describes the Hamiltonian $H$ by the connectivity matrix $A_T$. This suggestion is motivated by the similarity of the master equation for the CTRW and the Schrödinger equation for the transition amplitudes $\alpha_{mn}(t) = \langle m | \exp(-iHt) | n \rangle$, reading [11]:

$$\frac{d}{dt} \alpha_{mn}(t) = -i \sum_l H_{ml} \alpha_{ln}(t).$$

(1.13)

Therefore, apart from the factor of $i$, the mathematical structure of the master equation and the Schrödinger equation for the transition amplitudes is the same. The major difference however, is that the transition probabilities are obtained by squaring the amplitudes. They are therefore sensitive to quantum interference effects between the different waves that propagate on the network and can lead to different results. More formally, the transition probability for going from node $n$ to node $m$ in a time $t$ is given by [11]:

$$\pi_{m,n}(t) = |\alpha_{mn}(t)|^2.$$

(1.14)

Denoting the eigenvalues of $H$ by $E_n$ and its corresponding eigenstates by $|\psi_n\rangle$, one obtains the following useful expression [11]:

$$\pi_{m,n}(t) = \sum_k e^{-iE_k t} \langle m | \psi_k \rangle \langle \psi_k | n \rangle^2.$$

(1.15)
The CTQW does not have a well-defined longtime limit as the CTRW due to the unitary evolution. In order to compare the behaviour at long times for both cases one needs to consider the long-time average \[\chi_{m,n}(t) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \pi_{m,n}(t) \, dt = \sum_{ab} \delta_{E_a,E_b} \langle m|\psi_a \rangle \langle \psi_a|n \rangle \langle n|\psi_b \rangle \langle \psi_b|m \rangle. \tag{1.16}\]

The efficiency of both the CTRW and the CTQW can be studied by considering the return probabilities \(p_{jj}(t)\) and \(\pi_{jj}(t)\) respectively. If the initial decay of the return probabilities is fast, the excitation moves quickly from the starting node to the rest of the network. A slow decay indicates that the excitation can only propagate slowly through the network. To make a global statement on the efficiency, one considers the average return probabilities \[\bar{p}(t) = \frac{1}{N} \sum_j p_{jj}(t), \quad \bar{\pi}(t) = \frac{1}{N} \sum_j \pi_{jj}(t). \tag{1.17}\]

The average return probability for the CTRW can be written as \[\bar{p}(t) = \frac{1}{N} \sum_n e^{-\lambda_n t}, \tag{1.18}\]

where the \(\lambda_n\) are the eigenvalues of the transfer matrix \(T\). For the CTQW one finds:

\[\bar{\pi}(t) = \frac{1}{N} \sum_j |\alpha_{jj}(t)|^2 \geq \left| \frac{1}{N} \sum_j \alpha_{jj}(t) \right|^2 = \left| \frac{1}{N} \sum_n e^{-iE_n t} \right|^2. \tag{1.19}\]

It follows that the average return probability for the CTQW is an oscillating function, in contrast to the CTRW. In the long-time limit it will oscillate around its corresponding long-time average:

\[\bar{\pi} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt \bar{\pi}(t). \tag{1.20}\]

After this formulation of the CTQW, I want to shortly return to the exact cover problem that was mentioned before. In their article, Farhi and Gutmann showed that for a certain class of trees, the exact cover problem could be solved exponentially faster as compared to the corresponding classical method [10]. That this is not always the case, has for example been shown in Refs. [26, 27]. In the rest of this thesis, I will show various examples of the differences between the CTRW and CTQW on the transport efficiency in networks.
1.2 Quantum dynamical maps

1.2.1 Open quantum systems

Aside from either purely classical transport on networks, described the CTRW, or purely unitary dynamics, as described by the CTQW, it is also possible and useful to consider more general forms of transport on networks. This can be done, for example, by placing the network in an external environment, such as a thermal reservoir or a specific type of solvent. In this section I will closely follow the contents of sections 3.1 and 3.2 of Ref. [18].

More formally, one considers a system $S$ and an environment $B$ that are coupled to each other and refer to $S$ as an open system. Usually it is assumed that the total system $S + B$ is a closed system, in the sense that the dynamics on it can be described by a Hamiltonian $H^1$. However, due to the interactions between $S$ and $B$ it is in general not possible to describe the dynamics on $S$ with a Hamiltonian. The dynamics on the subsystem $S$ is usually referred to as reduced dynamics. The purpose of this section is to introduce the mathematical framework that is needed to properly describe the reduced dynamics on $S$, in the case where the dynamics is Markovian. The exact definition of the latter for quantum systems will be provided later.

The Hilbert space of the total system is denoted by $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B$, where $\mathcal{H}_S$ is the Hilbert space of the system and $\mathcal{H}_B$ the Hilbert space of the environment. The Hamiltonian that describes the unitary dynamics on $\mathcal{H}$ is written as:

$$H = H_S \otimes I_B + I_S \otimes H_B + H_I,$$

(1.21)

where $H_S$ is the Hamiltonian of the open system $S$, $H_B$ the Hamiltonian of the environment $B$ and $H_I$ the Hamiltonian that describes the interactions between $S$ and $B$. Often, the environment consists of a large number of degrees of freedom and one is only interested in their effect on the reduced dynamics on $S$ through the interaction term $H_I$. This means one is only interested in measuring operators of the form $A \otimes I_B$, with $A$ an operator acting on the Hilbert space $\mathcal{H}_S$. The expectation value of such an operator is then given by:

$$\langle A \rangle = \text{tr}_S (A \rho_S),$$

(1.22)

where $\rho_S$ is the reduced density operator of the system. When $\rho$ is the density operator for the full system, it is defined by $\rho_S = \text{tr}_B (\rho)$. The reduced

\footnote{Note that the system $S$ does not have to be represented by a finite Hilbert space. Therefore $H$ is not written in bold face notation.}
density operator is thus obtained by tracing out all the degrees of freedom corresponding to the environment.

The dynamics of the density operator is given by the Liouville-von Neumann equation [24]:

\[
\frac{d\rho(t)}{dt} = -\frac{i}{\hbar} [H, \rho(t)].
\] (1.23)

In terms of the time-evolution operator \( U(t, t_0) = e^{-iH(t-t_0)/\hbar} \), the solution to this equation can be formulated as:

\[
\rho(t) = U(t, t_0)\rho(t_0)U^\dagger(t, t_0).
\] (1.24)

The reduced density operator can therefore be written as:

\[
\rho_S(t) = \text{tr}_B \{ U(t, t_0)\rho(t_0)U^\dagger(t, t_0) \}.
\] (1.25)

Unfortunately, this description still requires the full knowledge of the time evolution of the total system through the operator \( U(t, t_0) \). In most systems this is unfeasable. Therefore, certain approximations have to be made in order to obtain an equation of motion for the reduced density matrix that does not involve operators acting on other parts of the total system.

### 1.2.2 Quantum Markov processes

As described in section 1.1.2, classical Markovian transport can be characterized by the Chapman-Kolmogorov equation. Its integral formulation (Eq. 1.4) for the transition probabilities \( T_\tau(y_2|y_1) = P_{1|1}(y_2, t_2|y_1, t_1) \), with \( \tau = t_2 - t_1 \), represents the mathematical concept of a semigroup:

\[
T_{\tau+\tau'}(y_3|y_1) = \int dy_2 T_\tau(y_3|y_2)T_{\tau'}(y_2|y_1).
\] (1.26)

Since \( \tau \) can only take on positive values, i.e. \( \tau \geq 0 \), the set \( \{ T_\tau \} \) is referred to as a semigroup instead of as a group. Analogously, one can extend this property to quantum mechanical systems. The evolution of a quantum mechanical system is then called Markovian if it satisfies the semigroup property. Due to the unitarity of the time-evolution operator, it is easily seen that the time evolution of closed quantum systems is Markovian. For open quantum systems this is generally not true and it depends on the details of the interaction of the system with its environment. When the correlation times of the environment are small, one can neglect memory effects in the reduced dynamics and describe it with a dynamical semigroup.
Suppose that at $t = 0$ there exists no correlation between the system and environment, such that $\rho(0) = \rho_S(0) \otimes \rho_B$, where $\rho_S(0)$ is the reduced density operator of the system and $\rho_B$ the one of the environment, which is assumed to be fixed. The time evolution of the reduced density operator $\rho_S(t)$ can now be described by the following map:

$$\rho_S(0) \longrightarrow \rho_S(t) = V(t)[\rho_S(0)], \quad (1.27)$$

where $V(t)$ is defined as (c.f. Eq. (1.25)):

$$V(t)[\rho_S(0)] = \text{tr}_B \left\{ U(t, 0)(\rho_S(0) \otimes \rho_B)U^\dagger(t, 0) \right\}. \quad (1.28)$$

This map is also called a *dynamical map*. It can be shown that $V(t)$ is a completely positive map and that it is trace-preserving:

$$\text{tr}_S \{ V(t)[\rho_S(0)] \} = \text{tr}_S \{ \rho_S(0) \} = 1. \quad (1.29)$$

After constructing the dynamical maps $V(t)$ for every value of $t$ one obtains a one-parameter family $\{ V(t) \mid t > 0 \}$. Such a family constitute a dynamical semigroup when the following holds:

$$V(t_1)V(t_2) = V(t_1 + t_2), \quad t_1, t_2 \geq 0. \quad (1.30)$$

Under some general mathematical assumptions, it is possible to represent $V(t)$ as an exponential of a linear map $\mathcal{L}$ [28]:

$$V(t) = \exp(\mathcal{L}t). \quad (1.31)$$

One also refers to this linear map as the generator of the semigroup. This formulation leads to the following differential equation for the reduced density operator $\rho_S(t)$:

$$\frac{d\rho_S(t)}{dt} = \mathcal{L}[\rho_S(t)]. \quad (1.32)$$

This equation forms the generalization of the Liouville-von Neumann equation for $\rho_S(t)$. It has been shown by Gorini, Kossakowski, Sudarshan and independently by Lindblad that the most general form of the generator $\mathcal{L}$, for a finite $N$-dimensional Hilbert space of the reduced system $S$, is given by [28, 29]:

$$\mathcal{L}[\rho_S(t)] = -\frac{i}{\hbar}[\mathbf{H}, \rho_S(t)] + \sum_{k=1}^{N^2} \gamma_k \left[ L_k \rho_T(t) L_k^\dagger - \frac{1}{2} \left\{ L_k^\dagger L_k, \rho_S(t) \right\} \right]. \quad (1.33)$$
The operators $L_k$ form a basis of the Liouville space and the constants $\gamma_k$ satisfy $\gamma_k \geq 0$. Note that the Hamiltonian $H$ is in general not equal to the system Hamiltonian $H_S$, since it can contain effective unitary dynamics resulting from the coupling to the environment. The Lindblad equation is invariant under unitary transformations of the Lindblad operators:

$$\sqrt{\gamma_k} L_k \rightarrow \sqrt{\gamma'_k} L'_k = \sum_i u_{ki} \sqrt{\gamma_i} L_i.$$  \hspace{1cm} (1.34)

This property allows one, in principle, to arbitrarily choose a set of Lindblad operators. This may not result in physical results however, since the choice of operators still has to be validated against more microscopic models or experiments. On the other side, this freedom allows one to quickly construct phenomenological models for the physical problems that are studied. In this chapter a microscopic derivation of the Lindblad equation is not derived, but it can be found in Ref. [18].

For future applications, it is useful to introduce the dissipator $D$, defined as the dissipative part of the Lindblad equation (1.33):

$$D[\rho_S(t)] = \sum_{k=1}^{N^2} \gamma_k \left[ L_k \rho_S(t) A_k^\dagger - \frac{1}{2} \left\{ L_k^\dagger L_k, \rho_S(t) \right\} \right].$$  \hspace{1cm} (1.35)

In general, each of the terms in the dissipator results in decoherence and/or relaxation effects in the reduced dynamics. Furthermore, the Lindblad equation is relaxing, meaning that it always has a well-defined stationary/equilibrium state. Note that this is not the case for purely unitary dynamics.

### 1.3 Quantum stochastic walks

Having introduced the concept of a quantum Markovian process and its associated Lindblad equation, it is now possible to combine the continuous-time random and quantum walk in one mathematical framework. This was first done by Whitfield et al. and they coined it the quantum stochastic walk [12]. It is based upon the observation that the dissipator of the Lindblad equation, for a suitable choice of Lindblad operators, can describe a CTRW on a network spanned by an arbitrary basis of the Hilbert space of the reduced system. In this section, I will work out and generalize the concepts of Ref. [12] in detail.
1.3. Quantum stochastic walks

1.3.1 Formal description

Consider an arbitrary basis \{ |\alpha \rangle \} of the \(N\)-dimensional Hilbert space of the reduced system \(S\). Note that the basis in which the density operator is written is still the node-basis \{ |i \rangle \} of the network. Now consider Lindblad operators of the form \(L_{\alpha\beta} = |\alpha\rangle \langle \beta|\). By construction, they form a complete basis of the Liouville space of the reduced system and are orthonormal in the sense of the trace norm:

\[
(L_{\alpha\beta}, L_{\kappa\eta}) = \text{tr}_S \left\{ L_{\alpha\beta}^\dagger L_{\kappa\eta} \right\} = \text{tr}_S \left\{ |\beta\rangle \langle \alpha| |\eta\rangle \langle \kappa| \right\} = \delta_{\alpha,\kappa}\delta_{\beta,\eta}. \tag{1.36}
\]

Denote the term of the dissipator corresponding to the Lindblad operator \(L_{\alpha\beta}\) by \(D_{\alpha\beta}\), i.e.:

\[
D_{\alpha\beta}[\rho_S(t)] = L_{\alpha\beta}\rho_S(t)L_{\alpha\beta}^\dagger - \frac{1}{2} \left\{ L_{\alpha\beta}^\dagger L_{\alpha\beta}, \rho_S(t) \right\}, \tag{1.37}
\]
such that

\[
D_{\text{QSW}}[\rho_S(t)] \equiv D[\rho_S(t)] = \sum_{\alpha,\beta=1}^{N} \gamma_{\alpha\beta} D_{\alpha\beta}[\rho_S(t)]. \tag{1.38}
\]

Projecting \(D_{\alpha\beta}[\rho_S(t)]\) on the basis \{ |\alpha\rangle \} leads to:

\[
D_{\alpha\beta}[\rho_S(t)] = \sum_{\kappa,\eta} \langle \kappa | D_{\alpha\beta}[\rho_S(t)] | \eta \rangle \langle \kappa | \langle \eta |. \tag{1.39}
\]

The matrix elements are given by:

\[
\langle \kappa | D_{\alpha\beta}[\rho_S(t)] | \eta \rangle = \delta_{\kappa,\alpha}\delta_{\eta,\beta} \langle \beta | \rho_S(t) | \eta \rangle
- \frac{1}{2} \left( \delta_{\kappa,\beta} \langle \beta | \rho_S(t) | \eta \rangle + \delta_{\beta,\eta} \langle \kappa | \rho_S(t) | \beta \rangle \right). \tag{1.40}
\]

This implies, after relabeling part of the indices, that:

\[
D_{\alpha\beta}[\rho_S(t)] = \langle \beta | \rho_S(t) | \beta \rangle |\alpha\rangle \langle \alpha | - \frac{1}{2} \sum_{\kappa} \left( \langle \beta | \rho_S(t) | \kappa \rangle |\beta\rangle \langle \kappa | + \langle \kappa | \rho_S(t) | \beta \rangle |\kappa\rangle \langle \beta | \right). \tag{1.41}
\]

By extracting the diagonal part from the sum, this expression can be rewritten as:

\[
D_{\alpha\beta}[\rho_S(t)] = \langle \beta | \rho_S(t) | \beta \rangle |\alpha\rangle \langle \alpha | - \langle \beta | \rho_S(t) | \beta \rangle |\beta\rangle \langle \beta | - \frac{1}{2} \sum_{\kappa \neq \beta} \left( \langle \beta | \rho_S(t) | \kappa \rangle |\beta\rangle \langle \kappa | + \langle \kappa | \rho_S(t) | \beta \rangle |\kappa\rangle \langle \beta | \right). \tag{1.42}
\]

\(^{2}\)Note that, in contrast to Eq. (1.33), I use two indices on the Lindblad operators. This is done to make its dependence on the basis vectors \(|\alpha\rangle\) and \(|\beta\rangle\) more clear.
To study the physical implications of the equation above it is useful to focus on the populations in the basis $\{|\alpha\rangle\}$, i.e. the diagonal elements of the density matrix in this basis. These populations are thus defined as $P_\alpha(t) = \langle \alpha | \rho_S(t) | \alpha \rangle$. Consider now a time-evolution of these populations that is only determined by the dissipator, meaning that the contributions of the coherent (Hamiltonian) part of the Lindblad equation are neglected:

$$\frac{d}{dt} P_\kappa(t) = \langle \kappa | D_{\text{QSW}} | \rho_S(t) | \kappa \rangle = \sum_\alpha \gamma_\kappa \alpha P_\alpha(t) - \sum_\alpha \gamma_\alpha \kappa P_\kappa(t). \quad (1.43)$$

When the basis $\{|\alpha\rangle\}$ is the basis of eigenstates of the system Hamiltonian $H_S$, the equation above is equivalent to the Pauli Master equation, provided that the rate constants $\gamma_{\alpha\beta}$ satisfy detailed balance [18]. Generalizing this observation, it is seen that the dissipator of the QSW therefore describes a classical rate (hopping) process on the network spanned by the basis states $\{|\alpha\rangle\}$ and that the populations $P_\alpha(t)$ are interpreted as the probability to be on node $|\alpha\rangle$, given some initial condition $P_\alpha(0)$. This rate process is a CTRW if the rates satisfy detailed balance.

One also observes from Eq. (1.42) that the dissipator decouples the coherences (the off diagonal elements of the density matrix) in the basis $\{|\alpha\rangle\}$. Denoting these coherences as $C_{\kappa\eta}(t) = \langle \kappa | \rho_S(t) | \eta \rangle$ implies that:

$$\langle \kappa | D | \rho_S(t) | \eta \rangle = -\frac{1}{2} \sum_\alpha (\gamma_{\alpha\kappa} + \gamma_{\alpha\eta}) C_{\kappa\eta}(t). \quad (1.44)$$

The off diagonal matrix elements of the dissipator therefore induce a decay of the coherences $C_{\kappa\eta}(t)$. Their rate of decay is determined by both the transfer rates $\gamma_{\alpha\beta}$ of the CTRW and the rates $\gamma_{\alpha\alpha}$. The latter are referred to as dephasing rates, since they are only responsible for the decay of the coherences and not for incoherent population transfer. Note however that one must take care in interpreting this result. Because the basis $\{|\alpha\rangle\}$ is not equal to the site basis in which the density matrix is studied in, these dephasing rates $\gamma_{\alpha\alpha}$ cause both population transfer and dephasing in the site basis. Furthermore, populations and coherences are no longer decoupled in the dissipative part, leading to complicated dynamics. Nonetheless, this flexibility in choosing the basis on which the CTRW, induced by the environment, takes place may allow one to model physical systems whose system-environment interactions take on non-standard forms.

In the rest of this thesis however, the focus lies on the relation/difference between a CTQW and CTRW on a given network. Therefore, I choose
the basis for the environmentally induced CTRW to be the site basis \{\{|i\}\}. This is a different choice than the one usually encountered in the literature, where the basis of energy eigenstates of \(H_S\) is often taken. For this choice, the Lindblad equation for the QSW is equivalent to the Redfield equation in the secular approximation, which has been successfully applied to many different physical systems \([17, 9]\). The choice in this thesis may therefore provide additional fresh insight in the different types of transport occurring on networks.

As a final remark, I want to point out that it is possible to extend the Markovian nature of the QSW to non-Markovian dynamics. This can be done by using the time-convolutionless (TCL) master equation, which is a time-local perturbative expansion of the full Liouville-von Neumann equation \([18]\). The TCL master equation can be written in Lindblad form, but the transition rates \(\gamma_{mn}\) can be time-dependent and can even become negative. Precisely this negativity can cause non-Markovian dynamics in the system \([30]\). In Chap. 5, I will use a phenomenological TCL master equation with time-dependent dephasing rates to model energy transfer in light harvesting systems.

To summarize, the master equation for QSW in the site basis, assuming that the environment does not induce effective unitary dynamics (i.e. \(H = H_S\)), is given by:

\[
\frac{d\rho_S(t)}{dt} = -i\frac{\hbar}{\hbar}[H_S, \rho_S(t)] + D_{QSW}[\rho_S(t)]
\]

\[
= -\frac{i}{\hbar}[H_S, \rho_S(t)] + \sum_{mn} \gamma_{mn} \left[ L_{mn} \rho_S(t) L_{mn}^\dagger - \frac{1}{2} \{ L_{mn}^\dagger L_{mn}, \rho_S(t) \} \right],
\]

with \(L_{mn} = |m\rangle \langle n|\). The coherent part of the master equation describes the CTQW, while the dissipator \(D_{QSW}[\rho_S(t)]\) describes the CTRW.

### 1.3.2 Transition between the CTQW and CTRW

There exist multiple ways to approach the transition between the CTQW and the CTRW when using the QSW. The approach that was originally introduced by Whitfield et. al. was to introduce an interpolation parameter \(\alpha \in [0, 1]\) in the master equation:

\[
\frac{d\rho_\alpha(t)}{dt} = -i\frac{\hbar}{\hbar}(1 - \alpha)[H_S, \rho_\alpha(t)] + \alpha D_{QSW}[\rho_\alpha(t)].
\]

Note that instead of \(\rho_S(t)\), I write \(\rho_\alpha(t)\) to make the dependence on the interpolation parameter \(\alpha\) more explicit. When \(\alpha = 0\), the dissipative part
vanishes and the dynamics is purely unitary. On the other hand, when \( \alpha = 1 \), the coherent part is zero and the dynamics is completely described by the dissipator \( \mathcal{D}_{\text{QSW}}[\rho_S(t)] \). Since the dissipator decouples the populations and coherences (Eqs. (1.43), (1.44)), the dynamics of the populations is described by the master equation of a CTRW (Eq. 1.43), while the coherences decay to zero. When \( 0 < \alpha < 1 \), the dynamics is a mixture between the CTQW and the CTRW. Note that the intention of this interpolating parameter is to use it as a mathematical tool to understand the differences between quantum and classical transport on a given network and not as a parameter that one can freely adjust in a single system. Namely, it is hard to conceive that coupling the network to an environment could lead to such a convex combination of the coherent and dissipative part. One indeed expects that the coupling constants only influence the dissipative part of the master equation through the transition rates \( \gamma_{mn} \) and possibly also in the form of a Lamb shift contribution to the Hamiltonian \( H_S \), but most likely not in the way introduced above.

**Transition to the equilibrium state**

Studying the transition from the CTQW and the CTRW can also be approached by studying the relaxation to an equilibrium state. As noted before the CTQW has no well-defined equilibrium state due to its reversible nature, but the Lindblad equation for the QSW has in most cases an unique equilibrium state. This state \( \rho_{eq} \) is defined as [18]:

\[
\rho_{eq} = \lim_{t \to \infty} \rho_S(t) \quad \iff \quad \mathcal{L}[\rho_{eq}] = 0. \tag{1.47}
\]

Note that the existence of this state is only guaranteed if the following condition on the Lindblad operators \( L_k \) holds [18]:

\[
[X, L_k] = 0 \quad \forall k \quad \implies \quad X \sim I_S, \tag{1.48}
\]

where \( I_S \) is the identity operator and \( X \) an arbitrary linear operator acting on \( \mathcal{H}_S \). If one assumes that the stationary state \( \rho_B \) of the environment is in a thermal equilibrium at inverse temperature \( \beta = 1/k_B T \), it can be written in the form of the canonical equilibrium (Gibbs) distribution [18]:

\[
\rho_B = \frac{\exp(-\beta H_B)}{\text{tr}_B \{\exp(-\beta H_B)\}}. \tag{1.49}
\]

One expects, if the system is much smaller than the environment and if there are no quantum mechanical correlations between the system and the
environment, that the state of the system evolves to a thermal equilibrium state with the same temperature as the environment:

\[ \rho_{eq} = \frac{\exp(-\beta H_S)}{\text{tr}_S \{ \exp(-\beta H_S) \}}. \]  

(1.50)

For the secular Redfield equation, this can indeed be proven by using the specific form of the Lindblad operators and that the transition rates satisfy detailed balance [18]. From this it then follows that the equilibrium populations \( \mathcal{P}_\alpha \) in the eigenstate basis are given by the Boltzman distribution \( \mathcal{P}_\alpha \sim \exp(-\beta E_\alpha) \), where \( E_\alpha \) is the eigenvalue corresponding to the eigenstate \( |\alpha\rangle \) of \( H_S \). However, for the QSW this is no longer true. Even though the coherent part of the master equation annihilates \( \rho_{eq} \), i.e.

\[ -\frac{i}{\hbar} [H_S, \rho_{eq}] = 0, \]

(1.51)

the dissipator \( \mathcal{D}_{QSW} \) does not. On the other hand, the equipartition state

\[ \rho_{ep} = \frac{1}{N} \mathbb{1}_S = \frac{1}{N} \sum_k |k\rangle \langle k|, \]

(1.52)

lies in the kernel of \( \mathcal{D}_{QSW} \), which can be shown in a straightforward way. Namely, the offdiagonal part of the dissipator (Eq. 1.44) reduces to:

\[ \langle m|\mathcal{D}_{QSW}[^{\rho_{ep}}]|n\rangle = -\frac{1}{2} \sum_k (\gamma_{km} + \gamma_{kn}) \langle m|\rho_{ep}|n\rangle = 0, \]

(1.53)

while the diagonal part of the dissipator (Eq. 1.43) becomes:

\[ \langle m|\mathcal{D}_{QSW}[\rho_{ep}]|m\rangle = \sum_k \gamma_{mk} \langle k|\rho_{ep}|k\rangle - \sum_k \gamma_{km} \langle m|\rho_{ep}|m\rangle = \frac{1}{N} \sum_k (\gamma_{mk} - \gamma_{km}) = 0. \]

(1.54)

The last line is true because I assume that there is no onsite disorder present in the Hamiltonian \( H_S \). This in turn implies that the detailed balance condition on the rates \( \gamma_{mn} \) reduces to \( \gamma_{mn} = \gamma_{nm} \). The equilibrium state of the dissipator is therefore the same as the equilibrium state of the CTRW, further corroborating the statement that the environment induces a CTRW on the network.

Note however that one cannot deduce the kernel of the Lindblad generator \( \mathcal{L} \) by knowing the kernels of the coherent and dissipative part seperately. In
general, this can only be done by analyzing the symmetries of the system in order to find a connection, or by performing a brute-force computation of all the eigenvectors of the full generator $\mathcal{L}$. Later in this thesis, the equilibrium state of the QSW will be investigated for a special cases.
Chapter 2

Sources and drains

2.1 Absorption processes

Consider a network consisting of $N$ nodes and an excitation that is moving on it, either by performing a continuous-time random walk, a continuous-time quantum walk or, more generally, a quantum stochastic walk. In many realistic physical systems it may occur that such an excitation decays or that it gets absorbed. A decay of the excitation can happen, for example, through a radiative process or by exciton recombination\textsuperscript{1}. Alternatively, it can happen that the excitation is absorbed at a particular node of the network. This occurs for instance if a chemical reaction takes place at that node or, for example, in light-harvesting systems where the excitation is absorbed into the reaction center [31].

2.1.1 Absorption in the CTRW

In this chapter the focus lies on absorption processes where the excitation can only vanish on certain nodes. These nodes are referred to as absorbing nodes or trap nodes. Suppose that there are $M$ absorbing nodes out of the $N$ total nodes in the network. The set of these absorbing nodes is denoted as $\mathcal{M}$. Consider now a CTRW on the network that is described by the master equation:

$$\frac{d\tilde{p}(t)}{dt} = T\tilde{p}(t),$$

(2.1)

\textsuperscript{1}An exciton can be considered as an electron-hole pair in a solid. Exciton recombination is the process where the electron and the hole meet and annihilate each other.
where \( \vec{p}(t) \) is the vector of the probabilities \( p_n(t) \) that represent the probabilities for being on node \( n \) at time \( t \) (see Eq. 1.8). One can now introduce the following trapping operator [11, 7]:

\[
\Gamma = \sum_{m \in M} \Gamma_m |m\rangle \langle m|.
\] (2.2)

The constants \( \Gamma_m \) represent the rates at which the excitation is absorbed at site \( m \) and they are assumed to be positive (\( \Gamma_m > 0 \)). In the following however, the range of the sum will be extended to include all the nodes of the network and to allow the constants \( \Gamma_m \) to be zero if node \( m \) is not a trap node. To include the effects of trapping in the CTRW, one modifies the transfer matrix \( T \) to \( T' = T - \Gamma \) [11]. The master equation, Eq. (2.1), then becomes:

\[
\frac{d\vec{p}(t)}{dt} = (T - \Gamma)\vec{p}(t),
\] (2.3)

and more explicitly for the components of \( \vec{p}(t) \):

\[
\frac{dp_n(t)}{dt} = \sum_m T_{nm} p_m(t) - \Gamma_n p_n(t).
\] (2.4)

From the equation above it follows that the total probability is not conserved:

\[
\frac{d}{dt} \sum_n p_n(t) = \sum_{n,n'} T_{nn'} p_{n'}(t) - \sum_n \Gamma_n p_n(t)
\]

\[
= \sum_{n'} p_{n'}(t) \left( \sum_n T_{nn'} \right) - \sum_n \Gamma_n p_n(t)
\]

\[
= - \sum_n \Gamma_n p_n(t),
\] (2.5)

since the transfer matrix \( T \) satisfies the relation \( \sum_n T_{nn'} = 0 \) for all \( n' \). This problem can be repaired by introducing an additional node \( |N + 1\rangle \) to the network, playing the role of the drain into which the excitation gets absorbed. Formally, the probability to be in this state is defined as:

\[
p_{N+1}(t) = 1 - \sum_{n=1}^{N} p_n(t),
\] (2.6)

and from Eq. (2.5) it follows that its time evolution is given by:

\[
\frac{dp_{N+1}(t)}{dt} = - \frac{d}{dt} \sum_{n=1}^{N} p_n(t) = \sum_{n=1}^{N} \Gamma_n p_n(t).
\] (2.7)
The transfer matrix $T$ has the property that it is a negative semi-definite matrix, meaning that all its eigenvalues $\lambda_n$ satisfy $\lambda_n \leq 0$. Since all the absorption rates $\Gamma_m$ are positive, it can be shown that all the eigenvalues of $T' = T - \Gamma$ are negative [7]. When the rates $\Gamma_m$ are small compared to the transition rates between the nodes, this easily follows from a perturbative viewpoint. Namely, in Dirac notation, the first order correction $\lambda_n^{(1)}$ to the $\lambda_n$ is given by:

$$\lambda_n^{(1)} = \lambda_n - \langle \psi_n | \Gamma | \psi_n \rangle = \lambda_n - \sum_m \Gamma_m | \langle \psi_n | m \rangle |^2 < 0,$$

(2.8)

where $| \psi_n \rangle$ is the eigenstate of the unperturbed transfer matrix $T$ with eigenvalue $\lambda_n$. Note that this perturbative argument works because the transfer matrix is assumed to be symmetric. The result above implies that, in the long-time limit, the excitation is completely absorbed by the drain:

$$\lim_{t \to \infty} p_n(t) = \lim_{t \to \infty} \sum_k e^{-\lambda_k t} \langle n | \psi_k' \rangle \langle \psi_k' | p(0) \rangle = 0, \quad n \neq N + 1$$

(2.9)

where $| \psi_k' \rangle$ is the eigenstate of $T'$ with eigenvalue $-\lambda_k'$.

With the knowledge that the excitation is always completely absorbed, an important question that one can ask is how long this process takes. One way to quantify this is to consider the mean survival probability $P_M(t)$, where the index $M$ refers to the total number of trap nodes in the network. It is defined as follows [11]:

$$P_M(t) = \frac{1}{N} \sum_{k,j} p_{kj}(t),$$

(2.10)

where $p_{kj}(t)$ is equal to the probability $p_k(t)$ given that $p_k(0) = \delta_{kj}$. The mean survival probability is therefore the probability that the excitation remains in the network, averaged over all the possible initial conditions. One can obtain an approximate expression for $P_M(t)$ if the smallest eigenvalue $-\lambda_1'$ of the transfer matrix $T'$ is well separated from the rest. This condition implies, for intermediate to long times, that $P_M(t)$ is described by a single decaying exponential. Upon using the expansion of $p_{kj}(t)$ in the eigenfunctions $| \psi_k' \rangle$ of $T'$, one indeed finds [11]:

$$P_M(t) = \frac{1}{N} \sum_n \sum_{k,j} e^{-\lambda_n' t} \langle k | \psi_n' \rangle \langle \psi_n' | j \rangle$$

$$\approx \frac{1}{N} e^{-\lambda_1' t} \left| \sum_k \langle k | \psi_1' \rangle \right|^2.$$

(2.11)
2.1. Absorption processes

2.1.2 Absorption in the CTQW

Absorption processes in quantum mechanical systems, for which the time evolution is described by the CTQW, can be formulated in a similar fashion as for the classical case (CTRW). To recall from the previous chapter, the Hamiltonian $H$ of the CTQW is obtained by identifying it with the transfer matrix $T$ of the CTRW, i.e. $H = -T$. This prescription, however, fails if one tries to include the effects of absorbing nodes into the CTQW. Namely, setting $H = -T' = -(T - \Gamma)$ merely leads to a change in the frequencies of the excitation and not to a decay. It is also similar to introducing static disorder in a tight-binding model by modifying the diagonal part of the Hamiltonian. The main idea now is to introduce the following altered prescription [32, 11]:

$$H = T - i\Gamma \equiv H_0 - i\Gamma.$$  (2.12)

In the equation above, $H_0$ is the Hamiltonian of the CTQW without any traps. Since the extra term to the Hamiltonian is purely imaginary, $H$ becomes a non-Hermitian matrix. It has $N$ complex eigenvalues $E_k = \epsilon_k - i\gamma_k$, where $\epsilon_k$ is the real part of $E_k$ and $\gamma_k$ its imaginary part. Due to the non-Hermiticity, the left and right eigenstates $|\Phi_k\rangle$ resp. $\langle \Phi_k|$ of $H$ are no longer equivalent, but for most physical systems one can assume that they form a complete and bi-orthonormal set of states [33]:

$$\sum_k |\Phi_k\rangle \langle \Phi_k| = \mathbb{I}_N, \quad \langle \Phi_k| \Phi_l\rangle = \delta_{kl}. \quad (2.13)$$

Exactly the imaginary parts of the complex eigenvalues $E_k$ of $H$ are responsible for the decay of the wavefunction. This decay is then interpreted as an absorption effect. Consider for example a (n) (right) eigenstate $|\Phi_k\rangle$ of $H$ for which the eigenvalue $E_k$ has a nonzero imaginary part $\gamma_k$. Its time evolution is then given by:

$$U(t, t_0) |\Phi_k\rangle = e^{-iE_k t} |\Phi_k\rangle = e^{-i(\epsilon_k - i\gamma_k) t} |\Phi_k\rangle = e^{-\gamma_k t} e^{-i\epsilon_k t} |\Phi_k\rangle . \quad (2.14)$$

Since the imaginary parts $\gamma_k$ are usually positive, it will decay to zero for $t \to \infty$. The positivity of the $\gamma_k$ can again be inferred from a perturbative argument, provided that the absorption rates are small compared to the transition rates appearing in $H_0$ [27]. The first order correction to the eigenvalues $E_k$ is given by:

$$E_k \approx E_k^{(0)} + E_k^{(1)} = E_k^{(0)} - i \sum_{m \in \mathcal{M}} \Gamma_m | \langle m | \Phi_k^{(0)} \rangle |^2. \quad (2.15)$$
2.1. Absorption processes

The superscript (0) refers to the unperturbed Hamiltonian $H_0$. This result is almost identical to the one that was obtained before for the CTRW (Eq. 2.8). Since the components of the eigenstates $|\Phi_k^{(0)}\rangle$ are real valued, the imaginary part of the eigenvalues $E_k$ is only determined by the perturbative correction. The decay of the wavefunction is thus determined by the total overlap of the unperturbed eigenstates with the sites that are connected to the trap.

Similar to the CTRW, one can introduce the mean survival probability, denoted as $\Pi_M(t)$. It is defined as follows [32]:

$$
\Pi_M(t) = \frac{1}{N} \sum_{k,j} \pi_{kj}(t). \quad (2.16)
$$

The mean survival probability can be written as a function of the imaginary parts $\gamma_l^2$ [32]:

$$
\Pi_M(t) = \frac{1}{N} \sum_{l=1}^{N} e^{-2\gamma_l t}. \quad (2.17)
$$

There is an interesting observation that follows from the result above. First, the decay of $\Pi_M(t)$ is only determined by the imaginary parts $\gamma_l$, while the decay of $P_M(t)$ is determined by the full eigenvalues of $T'$. In particular, this can lead to a non-zero stationary value of $\Pi_M(t)$. This purely quantum mechanical effect does not occur in the CTRW, since for the latter, the mean survival probability always decays to zero, see Eq. (2.9). Suppose for instance that for some $k$ it holds that $\gamma_k = 0$. This happens when $\langle \Phi_k^{(0)} | m \rangle = 0$ for all $m \in \mathcal{M}$. Eq. (2.17) then reduces to:

$$
\Pi_M(t) = \frac{1}{N} + \frac{1}{N} \sum_{l\neq k} e^{-2\gamma_l t}. \quad (2.18)
$$

Below, a short derivation of the form of $\Pi_M(t)$ in Eq. (2.17) is given. Upon using the definition $\pi_{kj}(t) = |\alpha_{kj}(t)|^2$, see Eq. (1.15), it follows that:

$$
\Pi_M(t) = \frac{1}{N} \sum_{k,j} \alpha_{kj}^*(t) \alpha_{kj}(t)
= \frac{1}{N} \sum_{k,j} \sum_{l,l'} e^{-i(E_l - E_{l'}) t} \langle j | \Phi_l \rangle \langle \Phi_l | k \rangle \langle k | \Phi_{l'} \rangle \langle \Phi_{l'} | j \rangle. \quad (2.19)
$$

Note that this expression is slightly different from the one used in Ref. [32]. Here, I sum over all possible initial conditions, instead of only summing over the initial conditions that are not trap nodes.
By using the completeness relation $\sum_k |k\rangle \langle k| = \mathbb{I}_N$ two times, I then obtain:

$$\Pi_M(t) = \frac{1}{N} \sum_{l,l'} e^{-i(E_l - E_{l'})t} \langle \Phi_{l'} | \Phi_l \rangle \langle \Phi_l | \Phi_{l'} \rangle = \frac{1}{N} \sum_l e^{-2\gamma_l t}. \quad (2.20)$$

### 2.2 Modelling sources and drains with the QSW

To review: I have formulated how to incorporate absorption effects in both the CTRW and the CTQW. This is done by introducing a trapping operator $\Gamma$ that is proportional to the projectors of the sites on which the absorption can take place. A similar procedure can be used to include absorption effects in the quantum stochastic walk (QSW). To see how this is done, it is useful to first consider the case of absorption for a CTQW, but now in the density matrix formalism.

#### 2.2.1 Drains

Consider now a CTQW on a network together with the trapping operator $\Gamma$. The Hamiltonian of this CTQW is then given by $H = H_0 - i\Gamma$, where $H_0$ is the Hamiltonian of the CTQW without absorption, see Eq. (2.12). Now consider the density matrix $\rho(t)$, given in terms of the time evolution operator $U(t,t_0) = \exp(-iH(t-t_0))$, i.e. $\rho(t) = U(t,t_0) \rho(t_0) U^\dagger(t,t_0)$. Differentiating with respect to $t$ leads to:

$$\frac{d\rho(t)}{dt} = -i \left( H\rho(t) - \rho(t)H^\dagger \right) \quad (2.21)$$

$$= -i( H_0 \rho(t) - \rho(t)H_0 - i\Gamma \rho(t) - i\rho(t)\Gamma)$$

$$= -i [H_0, \rho(t)] - \{\Gamma, \rho(t)\}. $$

The coherent evolution of the density matrix is therefore modified with an anticommutator corresponding to the trapping operator. Exactly this form on the right hand side is then used to modify the coherent part of the master equation of the QSW, Eq. (1.45). One then finds that:

$$\frac{d\rho_S(t)}{dt} = \mathcal{L}_{\text{coh}}[\rho_S(t)] + \mathcal{D}_{\text{QSW}}[\rho_S(t)]$$

$$= -i [H_0, \rho_S(t)] - \{\Gamma, \rho_S(t)\} + \mathcal{D}_{\text{QSW}}[\rho_S(t)]. \quad (2.22)$$
This formulation of the QSW also allows for an alternative description of absorption processes, by choosing a suitable Lindblad operator that models the transition from the network to the drain. Similar to the CTRW, where an extra node was introduced to the network to preserve the conservation of probability, one can also introduce such an extra node, denoted as $|N+1\rangle$, for the QSW. In order to prevent the excitation from getting back into the network, this node will be incoherently coupled to $M$ nodes of the network. The incoherent nature of the coupling implies that the drain is not coupled to the network through the Hamiltonian $H_S$, but that the dissipator is used to describe an incoherent hopping from the network to the drain. In other words, $H_{k,N+1} = 0$ for all nodes $|k\rangle$ of the original network. The total dimension of the systems Hilbert space is then $N+1$ and the density matrix of the network-drain system is then a $(N+1) \times (N+1)$ matrix.

The drain node $|N+1\rangle$ is coupled to node $|k\rangle$ of the network by introducing the Lindblad operator $L_{N+1,k} = |N+1\rangle \langle k|$ \cite{19}. This choice of the Lindblad operator is exactly of the general form in which the normal QSW is formulated, see Sec. 1.3.1. The coupling strength corresponding to this Lindblad operator will be denoted as $\Gamma_k$. The dissipator corresponding to $L_{N+1,k}$ is given by (see Eq. (1.42)):

$$D_{N+1,k}[\rho_S(t)] = \mathcal{P}_k(t)(|N+1\rangle \langle N+1| - |k\rangle \langle k|) - \frac{1}{2} \sum_{a \neq k} (C_{ka}(t) |a\rangle \langle a| + C_{ak}(t) |a\rangle \langle k|), \quad (2.23)$$

where $\mathcal{P}_k(t) = \langle k|\rho_S(t)|k\rangle$ and $C_{ka}(t) = \langle k|\rho_S(t)|a\rangle$ for $a \neq k$. The first term on the right hand side corresponds to a (incoherent) flow of population from node $|k\rangle$ to node $|N+1\rangle$, while the second term represents a decay of the coherences between $|a\rangle$ and $|k\rangle$. As before, let $\mathcal{M}$ be the set of nodes of the network that are connected to the drain. The master equation for the QSW then becomes \cite{19}:

$$\frac{d\rho_S(t)}{dt} = -i[H_0, \rho_S(t)] + D_{\text{QSW}}[\rho_S(t)] + \sum_{k \in \mathcal{M}} \Gamma_k D_{N+1,k}[\rho_S(t)]. \quad (2.24)$$

The similarity of both descriptions can be seen by rewriting the anticommu-
2.2. Modelling sources and drains with the QSW

tor \( \{ \Gamma, \rho_S(t) \} \) as follows [19]:

\[
- \{ \Gamma, \rho_S(t) \} = - \sum_{m \in M} \Gamma_m \{ |m\rangle \langle m|, \rho_S(t) \} - 2 \sum_{m \in M} \Gamma_m \left( \mathcal{P}_m(t) |m\rangle \langle m| + \frac{1}{2} \sum_{a \neq m} [\mathcal{C}_{ma}(t) |m\rangle \langle a| + \mathcal{C}_{am}(t) |a\rangle \langle m|] \right).
\]

Therefore it holds that [19]:

\[
-\frac{1}{2} \{ \Gamma, \rho_S(t) \} = \sum_{m \in M} \Gamma_m \mathcal{D}_{N+1,m}[\rho_S(t)] - \sum_{m \in M} \Gamma_m \mathcal{P}_m(t) |N + 1\rangle \langle N + 1|. \tag{2.27}
\]

On the subspace spanned by the nodes of the network both descriptions are equivalent. However, one has to take care when comparing them since the absorption rates are not equivalent. In the description of the CTQW, an absorption rate equal to \( \Gamma_k \) corresponds to an absorption rate of \( 2\Gamma_k \) in the Lindblad (QSW) formalism. The major difference between both descriptions is that the Lindblad formalism explicitly takes the transitions to the extra node \( |N + 1\rangle \) into account, while the description in terms of a non-Hermitian Hamiltonian does not.

Under certain general assumptions it is possible to write the density matrix in a block-diagonal form, where one block corresponds to the subspace spanned by the nodes of the network and where the other block is proportional to \( |N + 1\rangle \langle N + 1| \) [19]. To see this, consider the time evolution of \( \mathcal{C}_{N+1,k}(t) = \langle N + 1| \rho_S(t) |k\rangle \), for \( k \neq N + 1 \), following from the master equation of the QSW with absorption (Eq. 2.24):

\[
\frac{d}{dt} \mathcal{C}_{N+1,k}(t) = -i \sum_{a \neq N + 1} \mathcal{C}_{N+1,a}(t) H_{ak} - \frac{1}{2} \sum_{a \neq N + 1} \gamma_{ak} \mathcal{C}_{N+1,k}(t) - \frac{1}{2} \sum_{m \in M} \Gamma_m \mathcal{C}_{N+1,m}(t) \delta_{m,k} \tag{2.28}
\]

This provides a closed \( N \)-dimensional system of differential equations for the coherences \( \mathcal{C}_{N+1,k}(t) \), whose solution is determined by the initial conditions \( \mathcal{C}_{N+1,k}(0) \). In most cases, and especially for the cases considered in this thesis, the excitation is localized on a node \( |a\rangle \) on the network at \( t = 0 \), meaning that \( \rho_S(0) = |a\rangle \langle a| \). This implies that all coherences at \( t = 0 \) are zero.
and in particular that $C_{N+1,k}(0) = 0$ for all $k \neq 0$. The closed system of differential equations for the $C_{N+1,k}(t)$ then ensures that $C_{N+1,k}(t) = 0$ for all $k \neq N + 1$. By using the same argument, it also holds that $C_{k,N+1}(t) = 0$ for all $k \neq N + 1$. This in turn results in the following block-diagonal form of $\rho_S(t)$ [19]:

$$
\rho_S(t) = \begin{pmatrix}
\tilde{\rho}_S(t) & 0 \\
0 & \mathcal{P}_{N+1}(t)
\end{pmatrix},
$$

(2.29)

where $\tilde{\rho}_S(t)$ is the density matrix restricted to the subspace spanned by the nodes of the network and where $\mathcal{P}_{N+1}(t)$ is the population of the drain $|N+1\rangle$.

### 2.2.2 Sources

The framework of the QSW also allows one to include a source into the system, something which is not possible to do with the non-Hermitian Hamiltonian approach described before. A source is, similar to a drain, introduced as an extra node $|0\rangle$ to the network. The incoherent transitions from $|0\rangle$ to a node $|k\rangle$ of the network are again described by introducing a suitable Lindblad operator; in this case given by $L_{k0} = |k\rangle \langle 0|$ [19]. The dissipator that corresponds to this Lindblad operator is given by (see Eq. (1.42)):

$$
\mathcal{D}_{k0}[\rho_S(t)] = \mathcal{P}_0(t) \left( |k\rangle \langle k| - |0\rangle \langle 0| \right) - \frac{1}{2} \sum_{a \neq 0} (C_{0a}(t) |0\rangle \langle a| + C_{a0}(t) |a\rangle \langle 0|).
$$

(2.30)

The form of this dissipator is quite similar to the one for the drain. However, in this case there is a population flow from the source node $|0\rangle$ to the network, as indicated by the first term. The second term results in a decay of the coherences between $|0\rangle$ and the nodes of the network. The same argument that was used above, to show that in the presence of a drain the density matrix can be written in a block-diagonal form, can also be used here. This implies that in a source-network-drain system, the density matrix has the following form [19]:

$$
\rho_S(t) = \begin{pmatrix}
\mathcal{P}_0(t) & 0 & 0 \\
0 & \tilde{\rho}_S(t) & 0 \\
0 & 0 & \mathcal{P}_{N+1}(t)
\end{pmatrix},
$$

(2.31)

where again $\tilde{\rho}_S(t)$ is the density matrix restricted to the subspace spanned by the nodes of the network. Now let $S$ be the set of all the nodes in the network that are connected to the source. The rate at which the excitation
moves from the source to a node $|k\rangle \in S$ is denoted as $\Theta_k$. The full master equation, describing a network connected to both a source and a drain, is now given by [19]:

$$\frac{d\rho_S(t)}{dt} = L_{coh}[\rho_S(t)] + \mathcal{D}_{QSW}[\rho_S(t)] + \sum_{k \in \mathcal{M}} \Gamma_k \mathcal{D}_{N+1,k}[\rho_S(t)] + \sum_{k \in S} \Theta_k \mathcal{D}_{k0}[\rho_S(t)].$$

(2.32)

From the form of the dissipator $\mathcal{D}_{k0}[\rho_S(t)]$, Eq. (2.30), and the master equation above, it also follows that the time evolution of $\rho_0(t)$ is given by [19]:

$$\frac{d}{dt}\rho_0(t) = -\sum_{k \in S} \Theta_k \rho_0(t),$$

(2.33)

implying that

$$\rho_0(t) = e^{-\Theta t} \rho_0(0), \quad \Theta = \sum_{k \in S} \Theta_k.$$

(2.34)

The transport of the excitation from the source to the network is therefore just described by an exponential decay with the total rate $\Theta$, which is the sum of all the rates $\Theta_k$ corresponding to the transitions to the nodes in $S$. Note however, that this result is only valid if the initial condition does not include a non-zero coherence between the source node $|0\rangle$ and a node $|k\rangle$ of the network. If such an initial coherence would exist, it is not possible anymore to write the density matrix in a block-diagonal form, resulting in correlations between the source and network.

### 2.3 Expected survival time

In Sec. 2.1, I introduced the concept of the mean survival probability. For the CTRW it is denoted as $P_M(t)$ and for the CTQW it is denoted as $\Pi_M(t)$, where $M$ refers to the number of trap nodes in the network. It is also possible to extend this concept to the QSW, by using the description from the CTQW. The definition is as follows:

$$\Pi^{QSW}_M(t) = \frac{1}{N-M} \sum_{k \notin \mathcal{M}, \rho(0) \notin \mathcal{M}} \sum_{\rho(0)} P_k(t|\rho(0))$$

(2.35)

Here $P_k(t|\rho(0)) = P_k(t)$, given that at $t = 0$ it holds that $P_k(0) = \langle k|\rho(0)|k\rangle$. The set $\mathcal{M}$ is defined as:

$$\mathcal{M} = \{|m\rangle \langle m| \mid |m\rangle \in \mathcal{M}\}.$$
2.3. Expected survival time

It is the set of all the possible projectors corresponding to the trap nodes.

Instead of the mean survival probability, one can also study the expected survival time (EST). This is the expected amount of time that the excitation will reside in the network. For a network coupled to a source and a drain it is defined as follows\(^3\) [19]:

\[
\eta = \int_0^\infty dt \ (1 - P_{N+1}(t)) = \sum_{k=0}^N \int_0^\infty dt \ P_k(t). \tag{2.37}
\]

Since the population in the source can be described as an exponential decay, the EST can also be written as [19]:

\[
\eta = \int_0^\infty dt \ e^{-\alpha t} + \sum_{k=1}^N \int_0^\infty dt \ P_k(t) = \frac{1}{\beta} + \sum_{k=1}^N \int_0^\infty dt \ P_k(t). \tag{2.38}
\]

To be able to compute the EST without knowing the detailed solutions of the populations \(P_k(t)\), one can formulate the EST in terms of the Laplace transforms \(\tilde{P}_k(s)\) of the populations [19]:

\[
\eta = \lim_{s \to 0} \sum_{k=0}^N \int_0^\infty dt \ e^{-st}P_k(t) = \lim_{s \to 0} \sum_{k=0}^N \tilde{P}_k(s). \tag{2.39}
\]

Writing all the non-vanishing components of the density matrix in a \(N^2 + 2\) dimensional vector \(\tilde{\rho}_S(t)\) then leads to the following form of the master equation of the QSW:

\[
\frac{d\tilde{\rho}_S(t)}{dt} = \hat{L}\tilde{\rho}_S(t), \tag{2.40}
\]

with \(\hat{L}\) being the corresponding matrix form of the full generator of the QSW. Performing a Laplace transform on this set of differential equations results in the following equation [19]:

\[
(sI_{N^2+2} - \mathcal{L})\tilde{\rho}_S(s) = \tilde{\rho}_S(0), \tag{2.41}
\]

implying that [19]:

\[
\tilde{\rho}_S(s) = (sI_{N^2+2} - \mathcal{L})^{-1} \tilde{\rho}_S(0). \tag{2.42}
\]

The EST \(\eta\) can be used as a measure of the (in)-efficiency of transport on the network. A large value of \(\eta\) means that it takes a long time for the excitation

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\(^3\)This definition is related to the transport efficiency measures used in Refs. [34, 35].
to move to the drain and vise versa. It is also possible that $\eta$ becomes infinite. This happens when there is a finite probability that the excitation remains in the network, which can only happen if there is an eigenstate of the Hamiltonian $H_S$ that has no overlap with the nodes that are connected to the drain. Note that this effect is also reflected in the mean survival probability, which in this case attains a non-zero stationary value.
Part II

Part 2: Applications
Chapter 3

Networks with sources and drains

In the previous chapters I have introduced the theoretical tools that are needed to study both coherent, classical and dissipative transport on networks. In this chapter, I will use these tools to study a number of illustrative examples of transport on networks connected to a source and a drain.

First, I will focus on some concrete examples of simple networks with sources and drains, such as a monomer and a dimer. Then I will introduce the concept of a dark state for the QSW, in analogy with the corresponding concept in quantum optics [36, 37]. As the first non-trivial example, I will turn my attention to topologically disordered networks. These are networks for which positions of the nodes are chosen randomly and where the interactions depend on the distance between the nodes. Such networks have been studied before for the CTQW [38], but here I extend them to the QSW.

As a final example, I turn to a trimer network that has a clearly identifiable dark state [36, 39, 40]. In particular, I will show how the negative effects of this state on the transport efficiency can be circumvented by generalizing the source terms in the Lindblad equation. In this new description, the excitation can now move from the source to a delocalized state in the network. I then study the transport properties in the form of the EST, by looking at a set of different delocalized states of the trimer.

From the contents of this chapter, two articles have been published, see Refs. [20, 19].
3.1 Description of the QSW master equation

In the previous chapter, I introduced the quantum master equation for the QSW on a network that is connected to both a source and a drain. As a measure of the transport properties of the network, I also introduced the expected survival time (EST), which measures the average time that the excitation remains in the network.

In this chapter I modify the source-drain master equation, Eq. (2.32), to also include the interpolation parameter $\alpha$, see Eq. (1.46). This allows me to easily study the differences between coherent and classical transport. The full master equation is then given by:

$$\frac{d\rho_\alpha(t)}{dt} = (1 - \alpha)\mathcal{L}_{\text{coh}}[\rho_\alpha(t)] + \alpha\mathcal{D}_{\text{QSW}}[\rho_\alpha(t)] + \sum_{k \in \mathcal{M}} \Gamma_k \mathcal{D}_{N+1,k}[\rho_\alpha(t)] + \sum_{k \in \mathcal{S}} \Theta_k \mathcal{D}_{k0}[\rho_\alpha(t)]. \tag{3.1}$$

where instead of $\rho_S(t)$, I write $\rho_\alpha(t)$ to make the dependence on the interpolation parameter $\alpha$ more explicit. The ($\alpha$-dependent) EST is then defined as (Eq. (2.37)):

$$\eta(\alpha) = \sum_{k=0}^{N} \int_0^\infty dt \mathcal{P}_k(t, \alpha), \quad \mathcal{P}_k(t, \alpha) = \langle k | \rho_\alpha(t) | k \rangle. \tag{3.2}$$

In this chapter, I will assume that the transition rates appearing in the source and drain terms are given by $\Theta_k = \Theta$ and $\Gamma_k = \Gamma$ respectively. The dephasing rates $\gamma_{kk}$ (c.f. Eq. (1.45)) are assumed to be given by $\gamma_{kk} = \lambda$. Furthermore, I assume that the incoherent transition rates $\gamma_{km}$ for $k \neq m$ are estimated from Fermi’s golden rule [20, 19, 9]. This means that I assume that $\gamma_{km} = | \langle k | H_S | m \rangle |^2$. Finally, I always assume that the excitation starts in the source node, i.e. $\rho_\alpha(0) = |0\rangle \langle 0|$. 

3.2 Examples of the expected survival time

3.2.1 The monomer

Consider a network that consists of a single node $|1\rangle$ such that the source-network-drain system consists of the three nodes $|0\rangle, |1\rangle$ and $|2\rangle$. Now, the system Hamiltonian $H_S$ is simply given by:

$$H_S = |1\rangle \langle 1|.$$

\(3.3\)
According to the form of Eq. (2.31), the matrix form of the master equation then takes on a purely diagonal form, since the coherences between the system and the source and drain all vanish completely. For the diagonal elements of the density matrix I then find that [19]:

\[
\frac{d}{dt} \mathcal{P}_0(t, \alpha) = -\Theta \mathcal{P}_0(t, \alpha) \\
\frac{d}{dt} \mathcal{P}_1(t, \alpha) = \Theta \mathcal{P}_0(t, \alpha) - \Gamma \mathcal{P}_1(t, \alpha) \\
\frac{d}{dt} \mathcal{P}_2(t, \alpha) = \Gamma \mathcal{P}_1(t, \alpha).
\] (3.4)

Note that they do not depend on the parameters that appear in the dissipator for the QSW. This set of differential equations has the following solution [19]:

\[
\mathcal{P}_0(t, \alpha) = \exp(-\Theta t) \\
\mathcal{P}_1(t, \alpha) = \frac{\Theta}{\Theta - \Gamma} \left( \exp(-\Gamma t) - \exp(-\Theta t) \right) \\
\mathcal{P}_2(t, \alpha) = 1 - \frac{\Theta \exp(-\Gamma t) - \Gamma \exp(-\Theta t)}{\Theta - \Gamma}.
\] (3.5)

In Fig. (3.1), I show these solutions graphically. The transition rates that were used to create this figure are \( \Gamma = 1 \) and \( \Theta = 1/2 \). In this figure, one can see that the excitation moves completely from the source to the drain and that nothing remains in the monomer itself. This also implies that the EST takes on a finite value. To verify this, I compute the EST analytically as follows:

\[
\eta(\alpha) = \int_0^\infty dt \left[ \exp(-\Theta t) + \frac{\Theta}{\Theta - \Gamma} (\exp(-\Gamma t) - \exp(-\Theta t)) \right] \\
= \frac{1}{\Theta} + \frac{1}{\Gamma}.
\] (3.6)

It thus follows that the EST for a monomer depends solely on the transition rates corresponding to the source and drain. Higher values of these rates imply that the EST becomes smaller. This, in turn, means that transport through the monomer becomes more efficient.

### 3.2.2 A dimer with static diagonal disorder

Next, I turn to a more important and interesting example, namely a dimer. This is a network that consists of two nodes. Here I will focus on a dimer
with diagonal disorder, which means that the original Hamiltonian $H_0$ of the network is perturbed with a disorder operator $\Delta$, i.e. $H_{\text{dimer}} = H_0 + \Delta$ [41]. Dissipative dynamics on such networks have been studied before [42], but with a different form of the quantum master equation.

Here, I assume that the disorder matrix $\Delta$ only has diagonal entries. The Hamiltonian for the dimer can then be written as follows [42, 19]:

$$H_{\text{dimer}} = \begin{pmatrix} 0 & -V \\ -V & \Delta \end{pmatrix},$$

(3.7)

where $V$ is the coherent hopping rate between the two nodes. In contrast to the monomer, I have to make an assumption here to which nodes the source and drain are connected. To get the full effect of the energetic disorder, I choose to connect the source to node $|1\rangle$ and the drain to node $|2\rangle$. In this way, the excitation has to overcome an energy barrier before transferring to the drain.

It is possible to compute the exact solution for the EST by using the Laplace transform technique, see Eq. (2.39). By using Mathematica, it fol-
\begin{equation}
\eta(\alpha) = \frac{1}{\Theta} + \frac{2}{\Gamma} + \frac{1}{\alpha} \left[ \frac{1}{V} - \frac{f(\alpha)}{g(\alpha)} \right].
\end{equation}
\tag{3.8}

The functions $f(\alpha)$ and $g(\alpha)$ are in turn given by:

\begin{align*}
f(\alpha) &= 4(1 - \alpha^2)(2V\alpha + \Gamma + \alpha \Delta) \\
g(\alpha) &= 4V^2\alpha(2 + \alpha(3\alpha - 4)) + 4V(1 + 2(\alpha - 1)\alpha)(\Gamma + \alpha \Delta) \\
&\quad + \alpha(\Gamma^2 + 2\alpha\Gamma\Delta + (4 + \alpha(5\alpha - 8))\Delta^2).
\end{align*}
\tag{3.9}

Note that both $f(\alpha)$ and $g(\alpha)$ are independent of the transition rate $\Theta$ corresponding to the source. Therefore, the source only influences the EST by introducing the factor $1/\Theta$. Although this full expression is already quite complicated, it is possible to derive some interesting limiting cases. For example, when there is no diagonal disorder present, I find that:

\begin{equation}
\lim_{\Delta \to 0} \eta(\alpha) = \frac{1}{\Theta} + \frac{2}{\Gamma} + \frac{1}{V\alpha} - \frac{4(1 - \alpha)^2}{\alpha V(4 - 8\alpha + 6\alpha^2) + \alpha^2 \Gamma}.
\end{equation}
\tag{3.10}

In the fully coherent limit, the EST takes on the following form:

\begin{equation}
\lim_{\alpha \to 0} \eta(\alpha) = \frac{1}{\Theta} + \frac{8V(V - \Gamma) + \Gamma^2 + 4\Delta^2}{4V^2\Gamma},
\end{equation}
\tag{3.11}

while in the incoherent limit it becomes:

\begin{equation}
\lim_{\alpha \to 1} \eta(\alpha) = \frac{1}{\Theta} + \frac{2}{\Gamma} + \frac{1}{V}.
\end{equation}
\tag{3.12}

From these results, it follows that the EST for classical transport on a disordered dimer is completely determined by the hopping rate $V$ and the source and drain rates. In contrast, it follows that this is not true for coherent transport. There, the energetic disorder has a large influence on the EST. Larger values of $\Delta$ lead to a quick increase in the EST. This can also be seen in the contour plot of Fig. (3.3).

In Fig. (3.2), I show the EST for the case of vanishing diagonal disorder, i.e. for $\Delta = 0$. The different curves correspond to different values of the drain rate $\Gamma$. Here, I see that higher values of $\Gamma$ lead to smaller values of the EST. This means that transport is more efficient for large drain rates. From the limits in Eqs. (3.11) and (3.12) it follows that the EST is smaller in the coherent regime than in the classical limit. Additionally, the EST has a maximum for an intermediate value $\alpha_e$. For this value, transport is the
Figure 3.2: The EST $\eta(\alpha)$ of a dimer for various values of the drain rate $\Gamma$, with $V = 1$ and no energetic disorder. The source rate is chosen to be $\Theta = 0.5$. A slight adaptation of this figure has also been published in Ref. [19].

most inefficient. This value can be computed by differentiating Eq. (3.10). I then obtain:

$$\alpha_* = \frac{-\Gamma}{2V} \pm \frac{1}{\sqrt{6}V} (\Gamma + 2V).$$

(3.13)

By constraining $\alpha_*$ to $0 \leq \alpha_* \leq 1$, either the plus or minus solution has to be taken. From this constraint it also follows, in order for this solution to exist, that:

$$\Gamma \leq \frac{4}{\sqrt{6} - 2} V.$$

(3.14)

For the values used in Fig. (3.2), for example, this formula amounts to $\alpha_* = 0.81$ for $\Gamma = 0.1$, while $\alpha_* = 0.72$ for $\Gamma = 1.0$.

The numerical results for the EST in the presence of diagonal disorder are shown in Fig. (3.3). There, I show the EST in the form of a contourplot, where the difference between the level curves is equal to 0.5. The most important difference to Fig. (3.2) is that there is no local maximum of the EST for $\Delta \gtrsim 1$. Instead, in this regime the EST decays monotonically with increasing values of $\alpha$. This means that in that case, transport is the most efficient in the classical regime.
3.3. Topologically disordered networks

Figure 3.3: This contour plot shows the EST of a dimer as a function of the disorder strength $\Delta$ and $\alpha$, for $\Theta = \Gamma = 0.5$ and $V = 1$. The distance between the levels in this contour plot is chosen to be 0.5. The more outward lying contours have a higher value of the EST. This figure has also been published in Ref. [19].

3.3 Topologically disordered networks

After the detailed discussion about the properties of the EST, I now focus on a more relevant physical example, namely topologically disordered networks. These are networks where the positions of the nodes are distributed randomly in space. I will model these networks by placing its nodes randomly in a sphere of unit radius. The interactions between the nodes are modelled as (distance-dependent) dipole-dipole interactions. To study the transport efficiency, I connect a source to the north pole of the sphere and a drain to the south pole. Similar networks have also been studied in the literature. For example, Ref. [38] studied the CTQW on large topologically disordered networks with the focus on the scaling behaviour of the average survival probability. In Refs. [43, 44, 45], the authors considered a similar set-up, but they were interested in determining the individual configurations that lead to the most efficient transfer.
The Hamiltonian of a topologically disordered network

Consider a network of \( N \) nodes that are placed in a sphere of radius \( R \). Without loss of generality, I can assume that \( R = 1 \), since other values would merely lead to a rescaling of time due to a global rescaling of all the distances between the nodes in the sphere. On both the north and south pole of the sphere I place a node, denoted as \(|1\) resp. \(|N\). The other \( N - 2 \) nodes are placed randomly in the sphere. The source is connected to node \(|1\), while the drain is connected to node \(|N\). As was mentioned before, the interactions \( V_{kl} \) between the nodes are assumed to be dipole-dipole interactions, taking on the form \( V_{kl} \sim d_{kl}^{-3} \), where \( d_{kl} \) is the distance between node \( k \) and node \( l \). The matrix elements of the Hamiltonian then take on the following form [19]:

\[
\langle k | H_S | l \rangle = \begin{cases} 
-d_{kl}^{-3} & \text{for } k \neq l \\
\sum_{j \neq k} d_{jk}^{-3} & \text{for } k = l
\end{cases}.
\] (3.15)

In most physical models the site energies are independent of the transition rates between the nodes. Here, however, I have chosen to preserve the correspondence of the transfer matrix \( T \) of the CTRW with the Hamiltonian \( H_S \) of the CTQW, by assuming the relation

\[
\sum_{j} H_{jk} = 0, \tag{3.16}
\]

to hold. This is the same condition as described in Section 1.1.2, above Eq. (1.8). This point was also addressed in Ref. [41], which studied the CTQW on a ring with various types of disorder.

Since the positions of the nodes are chosen randomly, the Hamiltonian becomes a random matrix. To obtain a global picture of the transport dynamics, I will therefore focus on the transport properties of the ensemble averaged density matrix:

\[
\bar{\rho}_\alpha(t) = \frac{1}{\mathcal{R}} \sum_{r=1}^{\mathcal{R}} \rho^{(r)}_\alpha(t), \tag{3.17}
\]

where \( \mathcal{R} \) is the total number of realizations and \( \rho^{(r)}_\alpha(t) \) the density matrix corresponding to realization \( r \), obtained from Eq. (3.1).

### 3.3.1 Numerical results

For all the numerical results that will be discussed in this section, I assume that \( N = 7 \). For the total number of realizations, I take \( \mathcal{R} = 4000 \). Namely,
Figure 3.4: This figure shows the populations of a topologically disordered network with $N = 7$ nodes and $\Gamma = 1$. The panels (a) and (b) correspond to $\alpha = 0$, while the panels (c) and (d) correspond to $\alpha = 0.01$. Furthermore, panels (a) and (c) show the populations of node $j_1$ and $j_N$ as well as the sum of the populations of the remaining nodes. Panels (b) and (d) in turn, show the populations of the source and drain nodes. An altered version of this figure has also been published in Ref [19].

For this value the numerical errors in $\rho_\alpha(t)$ can be neglected [19]. The source rate is assumed to be $\Theta = 0.5$, although its precise value is not particularly important: its contribution to the EST is just a term equal to $1/\Theta$, as can be seen from Eq. (2.38).

In Fig. (3.4), I show the populations of the system for two different values of $\alpha$, namely $\alpha = 0$ and $\alpha = 0.01$. As predicted from Eq. (2.34), the source indeed decays exponentially with rate $\Theta$ (see panels (b) and (d)). I also observe an initially high population of the north pole (panels (a) and (c)).

An interesting observation arises from this figure. Namely, for purely coherent transport ($\alpha = 0$), I see a form of short-to-intermediate time localization, with approximately 23% of the population remaining in the network.
3.3. Topologically disordered networks

Figure 3.5: Total population of the source-network system for two special configurations: one where all the nodes lie on the equator of the sphere and one where all the nodes lie on a straight line. The populations are shown for $\alpha = 0$ and $\alpha = 0.01$. An adaptation of this figure has been published in Ref. [19].

after $t = 30$ (see Figs. 3.4(a) and 3.4(b)). Usually however, as time progresses there is still some population that transfers to the drain. Furthermore, in the ensemble-average eventually everything is transported. For finite values of $\alpha$, the localization effect disappears completely, as can be seen from 3.4(c) and 3.4(d) for $\alpha = 0.01$. Larger values of $\alpha$ lead to similar behaviour. The only difference is that transport is faster for larger $\alpha$.

In Fig. (3.5) I show two interesting individual realizations of the topologically disordered network. In the first configuration, all the nodes between the north and south pole are placed randomly on the equator of the sphere. In the other configuration, all the nodes lie on a straight line between the north and south pole. Due to the symmetry of the first configuration it holds that all the couplings between the poles and the nodes on the equator are equal. Therefore it actually happens that transport for $\alpha = 0$ is faster than for $\alpha = 0.01$, which is in contrast to the results for the ensemble average. This behaviour is not observed for the second configuration, since it doesn’t exhibit this symmetry.
In Fig. (3.6), I show on a log-linear plot, the total population of the network excluding the drain, i.e. $1 - \langle N + 1 | \hat{\rho}_\alpha(t) | N + 1 \rangle$. For $\alpha = 0$, I observe a power-law-like decay for intermediate times, scaling as $t^{-\beta}$ with $\beta \approx 0.21$. This is characteristic for quantum walks in topologically disordered networks [38]. The decay is only visible here in a small region due to the small number of nodes of the network. Already for small values of $\alpha$ this behaviour vanishes. In the incoherent limit, this ultimately leads to a purely exponential decay. By fitting the curve corresponding to $\alpha = 1$ to an exponential function, I find that it scales as $e^{-\mu t}$ with $\mu = 0.247$. In total, I can conclude from these results that the quantum mechanical localization of the excitation is already destroyed for very small couplings to the environment.

In Fig. (3.7), I show the EST for various values of the drain rate $\Gamma$. Since the localization of the excitation prevents efficient transport, as was already discussed before, the EST has indeed its maximal value at $\alpha = 0$. Larger couplings to the environment then lead to faster delocalization and in turn to a monotonic decay of $\eta(\alpha)$ with $\alpha$. I also observe that higher values of the drain rate $\Gamma$ lead to almost identical curves for the EST, but with a lower
3.3. Topologically disordered networks

Figure 3.7: The EST for the topologically disordered network for various values of the drain rate $\Gamma$. This figure also appears in Ref. [19].

Figure 3.8: Plot showing the EST of a topologically disordered network with $\Gamma = 0.5$ that is fitted to the EST of a disordered dimer. The fitting parameters are shown in the figure. A slight adaptation of this figure also appears in Ref. [19].
offset. To conclude, large values of $\alpha$ combined with large drain rates lead to the most efficient transfer through a topologically disordered network.

Upon comparing the EST of a topologically disordered network in Fig. (3.7) with the one of a dimer with diagonal disorder $\Delta$ in Fig. (3.3), I see that they show a similar decay when $\Delta \gtrsim 1$. This leads to the question if the EST of a topologically disordered network can be understood in terms of a disordered dimer. That this is indeed the case can be seen from Fig. (3.8). There, I have fitted the EST, for $\Gamma = 0.5$, to a dimer with the following parameters: $\Theta_d = 0.19$, $\Gamma_d = 1.23$, $V = 0.61$ and $\Delta = 1.8$. Note that I have included the subscript $d$ to distinguish the source and drain rates from those of the topologically disordered network. In performing this fit, I have only fitted $\Theta_d$, $\Gamma_d$ and $V$, since I have the freedom of choosing the disorder strength $\Delta$, as long as $\Delta \gtrsim 1$. Higher values of $\Delta$ then correspond to higher values of $\Gamma_d$, $\Theta_d$ and $V$. This can be understood by noting that to overcome a higher energy barrier, one must simultaneously increase both the source and drain rates. For other values of $\Theta$ and $\Gamma$ of the disordered network, the fit behaves in a similar way [19].

Therefore, I can conclude that the EST of a topologically disordered network can be well described by modelling the system as a disordered dimer. This then illustrates that one can study the transport efficiency of a large disordered network by reducing it to a dimer.

### 3.4 The effect of the initial state

In this section I will focus on networks that exhibit a dark state. This is a state in which the excitation can get trapped and after that does not take part in the transport anymore. In quantum optics and mesoscopic physics, this effect is also referred to as coherent population trapping [36, 39, 40, 18]. In particular, I will focus on a trimer network, for which the first and last node are not connected to each other. This is the simplest example of a network that has a dark state, provided that the site energies and couplings are chosen in a correct way [39, 46, 47, 48, 49]. Such a network is also referred to as a Lambda-system [18]. An example of this type of network can be a system of coupled quantum dots that are connected to two conducting leads [39, 40]. As before, I connect both a source and a drain to the network. The source is connected to both of the end nodes of the trimer, while the drain is connected to the middle node.

The dark state that occurs in this trimer causes the excitation to become
trapped inside the network. This inhibits transfer to the drain, especially in the purely coherent limit. There are a few standard solutions to this problem. First, one can introduce diagonal disorder on the nodes of the network [46, 47]. Another option is to couple the network to an environment, whose induced decoherence effects destroy the coherent nature of the dark state [50, 46]. In this section I will introduce a third method by making use of the flexibility in describing sources within the QSW. Namely, instead of just focusing on the situation where the source creates an initial excitation on a single node of the network, it is also possible to let the source induce a delocalized state in the network. In particular, if this delocalized state is exactly orthogonal to the dark state, this results in the complete absence of the effects of the dark state in the transport.

Next, I will first introduce the specific details of the QSW on such a Lambda system and will then illustrate how these other types of sources can be implemented. After that, I will show my numerical computations for this system. From the contents of this section, Ref. [20] has been published.

**Hamiltonian of the Lambda system**

Consider a Lambda system without diagonal and off-diagonal disorder. The Hamiltonian of this network can be written as follows:

\[
H_S = \begin{pmatrix}
  E & 0 & V \\
  0 & E & V \\
  V & V & E
\end{pmatrix}.
\]  

(3.18)

The eigenvalues \(\mu_n\) are given by:

\[
\mu_1 = E, \quad \mu_2 = E - \sqrt{2}V, \quad \mu_3 = E + \sqrt{2}V,
\]

(3.19)

and the eigenvectors \(|\xi_n\rangle\) by:

\[
|\xi_1\rangle = (|1\rangle - |2\rangle)/\sqrt{2}
\]

\[
|\xi_2\rangle = (|1\rangle + |2\rangle)/2 - |3\rangle/\sqrt{2}
\]

\[
|\xi_3\rangle = (|1\rangle + |2\rangle)/2 + |3\rangle/\sqrt{2}.
\]

(3.20)

Note that the state \(|\xi_1\rangle\) has no overlap with node \(|3\rangle\), being the node to which the drain is connected. This state can therefore be identified as a dark state for the transport process. From this point, I will denote this state as \(|D\rangle\) in order to make its nature more apparent.
3.4. The effect of the initial state

3.4.1 Initializing the system with a source

In chapter 2, I introduced the formalism that is needed to describe sources and drains that are coupled to a network. The Lindblad operator that models the transition from the source node $|0\rangle$ to a node $|k\rangle$ of the network was chosen to be $L_{k0} = |k\rangle \langle 0|$, see Sec. 2.2.2. More generally, it is also possible to extend this description by allowing for transitions from the source to a general state $|\psi\rangle = \sum_k a_k |k\rangle$ of the network. This can be described by the Lindblad operator $L_s = |0\rangle \langle \psi|$. Note that this state $|\psi\rangle$ can be a delocalized state of nodes that are not necessarily connected to each other in the network by a bond. The corresponding term in the Lindblad master equation, Eq. (3.1), is then simply given by:

$$L_s[\rho_\alpha(t)] = \Theta_sD_s[\rho_\alpha(t)], \quad (3.21)$$

with $\Theta_s$ the transition rate and $D_s[\rho_\alpha(t)]$ the dissipator corresponding to the Lindblad operator $L_s$, c.f. Eq. (1.37):

$$D_s[\rho_\alpha(t)] = L_s\rho_\alpha(t)L_s^\dagger - \frac{1}{2}\{L_s^\dagger L_s, \rho_\alpha(t)\}. \quad (3.22)$$
3.4. The effect of the initial state

It can be easily shown that this dissipator still allows for a block-diagonal description of the reduced density matrix $\rho_\alpha(t)$, see Eq. (2.31) [20].

There are now two interesting ways in which I can connect the source to the first two nodes of the Lambda system introduced above [20].

1. The first option is the version that has been considered before. Namely, I can connect the source to nodes $|1\rangle$ and $|2\rangle$ separately. These two transitions are then independent of each other, similar to transitions inside the network from one node to another. The terms in the master equation describing this process are given by (c.f. Eq (2.30)):

$$\mathcal{L}_{\text{source}}^{(1)}[\rho_\alpha(t)] = \frac{\Theta}{2} \mathcal{D}_{10}[\rho_\alpha(t)] + \frac{\Theta}{2} \mathcal{D}_{20}[\rho_\alpha(t)]$$

$$= \frac{\Theta}{2} \mathcal{P}_0(t,\alpha) (|1\rangle \langle 1| + |2\rangle \langle 2| - 2 |0\rangle \langle 0|). \quad (3.23)$$

Note that I have chosen the transition rate to be $\Theta_s = \Theta/2$. For this choice, the total transition rate from the source into the network is then given by $2\Theta_s = \Theta$. This in turn allows for simpler equations later on in this section and for a direct comparison to the option described next.

2. The second option is to connect the source to the delocalized state

$$|\psi\rangle = (|1\rangle + e^{i\phi}|2\rangle) / \sqrt{2}. \quad (3.24)$$

Note that when the phase $\phi$ equals to $\phi = \pi$, this state is equal to the dark state $|D\rangle$ of the Lambda system. The Lindblad term corresponding to this option then follows from Eq. (3.21):

$$\mathcal{L}_{\text{source}}^{(2)}[\rho_\alpha(t)] = \Theta \mathcal{D}_s[\rho_\alpha(t)]$$

$$= \mathcal{L}_{\text{source}}^{(1)}[\rho_\alpha(t)] + \frac{\Theta}{2} \mathcal{P}_0(t,\alpha) (e^{-i\phi} |1\rangle \langle 2| + e^{i\phi} |2\rangle \langle 1|). \quad (3.25)$$

This generator for the source thus consists of the generator for a source that corresponds to sourcing the two nodes independently, Eq. (3.23) plus some additional coherence terms, depending on the phase $\phi$.

An illustration of these two options is given in Fig. (3.9). In the next subsection I will study the EST for this system numerically and will explore the differences between these two different initializations of the system and their effect on the transport properties.
3.4.2 The expected survival time

After these definitions on how to construct sources that allow for transitions into delocalized states of the network, I will focus on studying the properties of the EST for both configurations mentioned above. The EST for the first configuration will be denoted as $\eta_I(\alpha)$ and the EST for the second configuration will be denoted as $\eta_{II}(\alpha)$. Suppose now, without loss of generality, that $E = V = 1$ for the Hamiltonian in Eq. (3.18) and that the drain rate $\Gamma$ is given by $\Gamma = 1$. The ESTs can then be written as follows [20]:

\begin{align*}
\eta_I(\alpha) &= \frac{1}{\Theta} + \frac{f(\alpha)}{g(\alpha)}, \quad (3.26) \\
\eta_{II}(\alpha) &= \frac{1}{\Theta} + \left[\frac{f(\alpha) - h(\alpha) \cos \phi}{g(\alpha)}\right]. \quad (3.27)
\end{align*}

Here, $h(\alpha) = 4(1 - \alpha)^2$ and

\begin{align*}
&f(\alpha) = 4 + \alpha(17 + 13\lambda) + 2\alpha^2[\lambda(\lambda - 8) - 19] + 3\alpha^2[11 + \lambda(9 + 2\lambda)], \\
g(\alpha) = 4\alpha(2 + \lambda) - \alpha^2(15 + 7\lambda) + \alpha^3[11 + \lambda(9 + 2\lambda)]. \quad (3.28)
\end{align*}

As a reminder, the constant $\Theta$ refers to the local dephasing rate appearing in the QSW master equation (Eq. (3.1)). Note that the form of $\eta_I(\alpha)$ is quite similar to the one of the dimer, see Eq. (3.8). From the equations above, it is now possible to deduce some general properties of both ESTs.

1. The EST $\eta_{II}(\alpha)$ depends in a simple way on the phase $\phi$ of the state $|\psi\rangle$. This functional dependence in the form $\cos \phi$ is a direct consequence of the form of the induced coherences in Eq. (3.25).

2. With the help of Mathematica, it can be shown that $-h(\alpha)/g(\alpha)$ is a monotonically decreasing function of $\alpha$. Furthermore, $h(\alpha)$ vanishes at $\alpha = 1$. This in turn implies that $\eta_I(\alpha) = \eta_{II}(\alpha)$ in the classical limit $\alpha \to 1$. Its limiting value is equal to $4 + 1/\Theta$. Physically, this limit can be understood by noting that the extra coherences that are created by the second configuration, have no influence on the population dynamics in this regime.

3. Since $-h(\alpha)/g(\alpha)$ decays monotonically it follows that, for $\phi \in [0, \pi/2)$ and $\phi \in (3\pi/2, 2\pi]$, $\eta_{II}(\alpha) < \eta_I(\alpha)$ and that for the other values of $\phi$ it holds that $\eta_I(\alpha) < \eta_{II}(\alpha)$.

4. In the purely coherent limit $\alpha \to 0$, it holds that $\eta_I(\alpha) = \infty$, while

\[ \lim_{\alpha \to 0} \eta_{II}(\alpha) = \begin{cases} 
\frac{1}{\Theta} + \frac{25 + 13\lambda}{8 + 4\lambda} & \text{for } \phi = 0 \\
\infty & \text{for } \phi \neq 0
\end{cases}. \quad (3.29) \]
3.4. The effect of the initial state

Figure 3.10: This figure illustrates the dependence of the EST $\eta_{II}(\alpha)$ on the phase $\phi$, for $\lambda = 1$ and a source rate of $\Theta = 0.5$. This figure has also been published in Ref. [20].

Apart from these general statements, it is hard to make more analytical predictions. Therefore, I illustrate the solutions for the ESTs in Fig. (3.10) and Fig. (3.11) to get a better picture of their behaviour. In the former, the cosine dependence of $\phi$ in $\eta_{II}(\alpha)$ is clearly visible for small values of $\alpha$. Additionally, the infinite value of the EST can be clearly seen for $\phi \neq 0$ and $\alpha = 0$. This infinity occurs here because for these values of $\alpha$ and $\phi$, the dark state is not influenced by the drain and is a stationary state of the system, see Eq. (3.29). This causes both ESTs to diverge when $\phi \neq 0$. However, when $\phi = 0$, the dark state is completely orthogonal to the initialized state $|\psi\rangle$. This then results in the absence of the dark state in the dynamics of the excitation and in a finite value of the EST, meaning that the excitation always gets completely transported to the drain. This behaviour can also be clearly seen in Fig. (3.11), where all curves diverge when $\alpha \to 0$, except when $\phi = 0$.

In Fig. (3.12) I show the dependence of the ESTs on the dephasing rate $\lambda$ for the interesting case $\phi = 0$. The most important feature in this figure is that for increasing dephasing rates, the EST $\eta_{I}(\alpha)$ decreases. The environmental noise thus enhances transport in this case, a feature also found
3.4. The effect of the initial state

in other systems [46, 51]. On the other hand, this effect does not occur for the second configuration. There, the EST is the smallest when there is no dephasing present. The optimal transport efficiency is thus reached for $\alpha = \lambda = 0$. This can be understood as follows: since only for these parameters the dark state is completely avoided, any environmental noise will cause this state to be mixed together with the other eigenstates of the system. This, in turn, causes a temporary blocking of the transport until enough time has passed such that most of the coherences have died out.

Another interesting feature that follows from this figure, is that the EST $\eta_{II}(\alpha)$ is always smaller than $\eta_I(\alpha)$ (for $-\pi/2 < \phi < \pi/2$), but that after some critical value $\alpha_c$, both curves coincide. The smaller the dephasing rate, the smaller the value of $\alpha_c$ becomes. As was already mentioned before, the environmental noise destroys the coherences between the nodes, which in turn removes the special properties due to the initialization with the source. When $\alpha$ is large, these decoherence processes happen quickly enough such that $\eta_I(\alpha) \approx \eta_{II}(\alpha)$.

The value of $\alpha_c$, for $\cos \phi > 0$, can be computed analytically by finding the maximum of $\eta_{II}(\alpha)$, since after this point it follows the curve of $\eta_I(\alpha)$, as
can be seen from Fig. (3.12). For the case $\phi = 0$, this expression becomes:

$$\alpha_c = \frac{4}{3+2\lambda} \left[ \frac{(2+\lambda)^3}{11+9\lambda+2\lambda^2} - \frac{1}{4} \right].$$ \hspace{1cm} (3.30)$$

To conclude: My results in this section show that initializing the system in a delocalized state that is exactly orthogonal to the dark state leads to faster transport than any other state of the form $|\psi\rangle = (|1\rangle + e^{i\phi} |2\rangle)/\sqrt{2}$ with a phase $\phi \neq 0$. This process is also robust against perturbations induced by environmental dephasing noise. Furthermore, it holds that initializing the system in this delocalized state always results in faster transport than independently initializing the system in the two corresponding delocalized states, provided that the phase $\phi$ of $|\psi\rangle$ satisfies $\cos \phi > 0$.

I expect that these results will also hold for larger networks that have subspaces of eigenstates that do not have any overlap with nodes connected to the drain, for example for fully connected networks as described in Ref. [46], for random networks as in Ref. [52] or for large ring-like structures as in Ref. [49].
Chapter 4

Entropy growth in the quantum stochastic walk

In this chapter, I study the properties of the von Neumann entropy associated to the reduced density matrix of the quantum stochastic walk\(^1\). In particular, I find that the entropy shows interesting scaling behavior for a large range of parameters and networks. In the classical limit, where the von Neumann entropy reduces to the Shannon entropy, it has been numerically shown in previous studies that it grows logarithmically in time [53]. The logarithmic growth rate was then found to be equal to half the spectral dimension related to the underlying network. This growth rate is more generally known as the information dimension. For a CTRW, the information dimension is therefore equal to half the spectral dimension.

Here, I show that this behavior also extends towards the quantum regime. In particular, I compute the von Neumann entropy for both the Sierpinski gasket and the linear chain and find that it also exhibits a similar logarithmic growth regime. This allows me to extend the definition of the information dimension to the QSW. Unlike for the CTRW, however, I find that the information dimension is not equal to the half the spectral dimension, but instead depends on the interpolation parameter \(\alpha\). Precisely this difference allows me to demonstrate the differences between quantum and classical transport on networks and to see at which point the crossover occurs.

In the first section of this chapter, I will introduce the concepts of the spectral- and information dimension for a CTRW and show how they are related to each other. Next, I will introduce both the Sierpinski gasket and the

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\(^1\)In contrast to the previous chapter, I only consider networks that are not connected to a source and a drain.
4.1 Scaling dimensions related to the CTRW

Fractal and spectral dimension

In this section I will introduce the concepts of the spectral dimension and the information dimension for a CTRW. These concepts arose originally from studying the dynamical properties of a CTRW in disordered systems, as for example in percolating systems or on fractal systems [8]. In contrast to Euclidean structures, where the mean square displacement follows \( \langle R^2(t) \rangle \propto t \) for all dimensions \( d \) [7], this is no longer true in general for disordered systems. There, the diffusion law has to be modified to [54]:

\[
\langle R^2(t) \rangle \propto t^{2/d_w},
\]

where \( d_w \geq 2 \) is the random walk dimension. When \( d_w > 2 \), the diffusion process is also called anomalous.

Consider now a CTRW on a network that possesses a fractal-like structure, which are networks that have the property of self-similarity. This means

![Figure 4.1: Illustration of the Sierpinski gasket of generation \( g = 3 \). This realization consists of \( N_3 = 15 \) nodes.](image)
that the network consists of a number of substructures similar to the network itself. A good example of a fractal structure is the Sierpinski gasket, obtained by subdividing a triangle into three smaller sub-triangles (See Fig. (4.1) for an illustration of the Sierpinski gasket of generation \( g = 3 \)). The Sierpinski gasket of generation \( g \) consists of \( N_g = 3^{(g-1) + 1}/2 \) nodes [54]. Precisely this fractal structure will be used in this chapter as an illustrative example.

One characteristic aspect of fractal structures is that their Hausdorff dimension \( d_f \), or fractal dimension, is not necessarily equal to the Euclidean dimension in which the fractal is embedded. For example, for the Sierpinski gasket, one finds that the Hausdorff dimension \( d_f \) is given by [54]:

\[
d_f = \frac{\ln P}{\ln S} = \frac{\ln 3}{\ln 2} \approx 1.5849,
\]

where \( P \) is the number of subdivisions of the triangle and \( S \) the corresponding scaling factor. Aside from being a static measure of the fractal itself, it also occurs in dynamical properties of the CTRW.

Consider for example the (ensemble-averaged) return probability to the origin, denoted as \( \bar{p}(t) \), c.f. Section 1.1.3 and Eq. (1.17). It can be shown that \( \bar{p}(t) \) can be written in terms of the density of states \( \mathcal{N}(E) \equiv \frac{1}{N} \sum_{n=1}^{N} \delta(E - E_n) \), where the \( E_n \) are the eigenvalues of the transfer matrix \( T \), as follows [54]:

\[
\bar{p}(t) = \int_{0}^{\infty} dE \mathcal{N}(E) \exp(-Et).
\]

Since the mean-square displacement scales as \( \langle R^2(t) \rangle \propto t^{2/d_w} \) (Eq. (4.1)), it follows that after a time \( t \), the random walker has approximately visited a volume \( \langle V(t) \rangle = \langle R^2(t) \rangle^{d_f/2} \sim t^{d_f/d_w} \) of the fractal. Therefore, the average return probability is found to scale as [54]:

\[
\bar{p}(t) \sim 1/\langle V(t) \rangle \sim t^{-d_f/d_w}.
\]

Upon using this expression in Eq. (4.3) above, one obtains the following scaling relation:

\[
\mathcal{N}(E) \sim E^{d_f/d_w-1}.
\]

For a normal Euclidean space in \( d \) dimensions, it can be shown that the density of states scales as \( \mathcal{N}(E) \sim E^{d/2-1} \). Comparing this result to the one above, leads to the definition of the spectral dimension \( d_s \):

\[
d_s = \frac{2d_f}{d_w}.
\]
In terms of the spectral dimension, the average return probability thus scales as:

\[ p(t) \sim t^{-d_s/2}. \]  

(4.7)

**Information dimension**

Next, I will focus on the information dimension associated to a CTRW. This concept was first introduced for a discrete-time random walk (RW) by Argyrakis [55, 56], and was later generalized (numerically) by Kozak et. al. [53] to the CTRW. To introduce the concepts, I will shortly review these results in this section and will provide some analytical results concerning the CTRW.

First, note that the spectral dimension for a RW can also be defined through the scaling behavior of the number \( S(\tilde{N}) \) of distinct sites that are visited [55]:

\[ S(\tilde{N}) \sim \tilde{N}^{d_s/2}, \]

(4.8)

where \( \tilde{N} \) denotes the number of steps that have been performed. This is a direct analogue of Eq. (4.4), since the number of distinct visited sites is proportional to the average volume that is visited. For this scaling relation, it makes no difference how many times the walker has visited a particular site. To collect this information, it is useful to study the Shannon information entropy \( I_{\tilde{N}} \) related to the random walk. It is defined as follows [55, 56]:

\[ I_{\tilde{N}} = - \sum_{k=1}^{S(\tilde{N})} P_k \ln P_k, \]

(4.9)

where \( P_k = i_k / \tilde{N} \) is the probability of visiting the \( k \)-th node and \( i_k \) the number of times node \( k \) has been visited. The information dimension \( d_I \) is now defined as [55]:

\[ d_I = I_{\tilde{N}} / \ln \tilde{N}. \]

(4.10)

The information dimension can be generalized to the CTRW by considering its associated continuous variant of the Shannon entropy [53]:

\[ I(t) = - \sum_n p_{nk}(t) \ln p_{nk}(t). \]

(4.11)

In the definition above, the sum runs over all the nodes of the network. Note that it is important to choose the initial condition \( k \) in the center of the
network, in order to avoid finite-size effects. The information dimension $d_{I}$ is now defined as the logarithmic growth rate of $I(t)$ with time [53]:

$$
d_{I} = \frac{I(t)}{\ln t}, \quad \text{when} \quad t \geq t_{I}.
$$

(4.12)

Here, $t_{I}$ is the initial spreading time that is needed before the walker transitions into the logarithmic growth regime.

For various fractal structures, in particular for the Sierpinski gasket, it has been shown that the probability distributions can be described by a stretched exponential scaling form, depending on $d_{s}$, $d_{f}$ and $d_{w}$ [57, 54]:

$$
p_{nk}(t) \sim t^{-d_{s}/2} r_{n}^{d_{f}-d} \exp \left[ -\left( \frac{r_{n}}{t^{1/d_{w}}} \right)^{u} \right], \quad \text{with} \quad u = d_{w}/(d_{w} - 1) \quad \text{and} \quad r_{n} \text{ the distance between node } n \text{ and the initial condition, node } k. \quad \text{Note that this scaling form is only valid when } r_{n} t^{-1/d_{w}} \gg 1. \quad \text{By using this scaling form, it is possible to derive the following expression for the Shannon entropy:}

$$
I(t) = -\sum_{n} p_{nk}(t) \ln p_{nk}(t)
$$

$$
\sim -\sum_{n} p_{nk}(t) \ln \left[ t^{-d_{s}/2} r_{n}^{d_{f}-d} \exp \left[ -\left( \frac{r_{n}}{t^{1/d_{w}}} \right)^{u} \right] \right]
$$

$$
= \frac{d_{s}}{2} \ln(t) \sum_{n} p_{nk}(t) - \sum_{n} p_{nk}(t) \ln \left( r_{n}^{d_{f}-d} \right) + t^{-u/d_{w}} \sum_{n} p_{nk}(t) r_{n}^{u}
$$

$$
= \frac{d_{s}}{2} \ln(t) - \langle \ln(\langle r^{d_{f}-d} \rangle) \rangle + t^{-u/d_{w}} \langle r^{u} \rangle. \quad \text{(4.14)}
$$

This means that, after some initial time has passed, $I(t)$ grows logarithmically with $t$:

$$
I(t) \sim \frac{d_{s}}{2} \ln(t). \quad \text{(4.15)}
$$

Therefore, it holds that the information dimension $d_{I}$ for a CTRW can be directly related to the spectral dimension $d_{s}$, provided that the scaling form in Eq. (4.13) is valid:

$$
d_{I} = d_{s}/2. \quad \text{(4.16)}
4.2 Scaling behaviour of the von Neumann entropy

Quantum Master equation

In this section, I will generalize the concepts that were introduced in the previous section to the quantum stochastic walk. To proceed, I write the master equation for the QSW, with interpolation parameter $\alpha$, as follows (see Eq. (1.46)):

$$\frac{d\rho_\alpha(t)}{dt} = (1 - \alpha) [H_S, \rho_\alpha(t)] + \alpha D_{QSW}[\rho_\alpha(t)] = (1 - \alpha) L_{CTQW}[\rho_\alpha(t)] + \alpha \left( L_{CTRW}[\rho_\alpha(t)] + L_{deph}[\rho_\alpha(t)] \right). \quad (4.17)$$

The generator $L_{CTQW}[\rho_\alpha(t)]$ describes the coherent part (CTQW) with Hamiltonian $H_S$, while the generator $L_{CTRW}[\rho_\alpha(t)]$ models the environmentally induced CTRW. Finally, $L_{deph}[\rho_\alpha(t)]$ describes a localized dephasing process for each node of the network. For the rest of this section, I assume that the excitation is initially localized on a single site $|k\rangle$ of the network, i.e. $\rho_\alpha(0) = |k\rangle \langle k|$. Furthermore, I assume that the dephasing rate is equal to $\lambda$ for all nodes of the network. As in the previous chapter, I assume that the incoherent transition rates follow from Fermi’s golden rule, that is $\gamma_{km} = |\langle k|H_S|m\rangle|^2$.

Information dimension for the QSW

In the previous section, the information dimension $d_I$ was defined through the Shannon information entropy $I(t)$. To generalize this concept to the QSW, I consider the von Neumann entropy $S_{vn}(t, \alpha)$, defined as:

$$S_{vn}(t, \alpha) = - \text{tr} \{ \rho_\alpha(t) \ln \rho_\alpha(t) \}. \quad (4.18)$$

In the limit $\alpha \to 1$, the dynamics is purely classical and therefore the von Neumann entropy reduces to the Shannon information entropy (Eq. (4.11)):

$$\lim_{\alpha \to 1} S_{vn}(t, \alpha) = - \lim_{\alpha \to 1} \text{tr} \{ \rho_\alpha(t) \ln \rho_\alpha(t) \} = - \sum_n p_n(t, 1) \ln p_n(t, 1) = - \sum_n p_{nk}(t) \ln p_{nk}(t) \quad (4.19)$$
where $P_n(t;1) = \lim_{\alpha \to 1} P_n(t,\alpha)$ with $P_n(t,\alpha) = \langle n | \rho_n(t) | n \rangle$, c.f. Sec. 1.3.1.

Because the von Neumann entropy is well defined for all values of $\alpha$ and contains the Shannon information entropy as a limiting case, I can define the information dimension $d_I(\alpha)$ for the QSW as follows:

$$S_{vn}(t, \alpha) \sim d_I(\alpha) \ln t, \quad t_I \leq t \leq t_{eq},$$

(4.20)

where $t_I$ is the initial time that is required before the logarithmic growth regime sets in and $t_{eq}$ the time when the excitation reaches its stationary state. Note that this definition is only valid provided that a logarithmic growth regime exists.

As for the CTRW, where the entropy $I(t)$ contains the information about the number of sites that have been visited, the von Neumann entropy can be interpreted as a measure for the spread of the excitation on the network. Initially, at $t = 0$, the excitation resides in a pure state and therefore $S_{vn}(0) = 0$. After some time, the excitation relaxes to its stationary state which is usually a maximally mixed state. There, the von Neumann entropy is equal to $S_{vn}(t, \alpha) = \ln N$ [18]. To make any statements about the behaviour in the intermediate-time regime it is useful to study a dimer system, since it is still simple enough to allow for analytical computations.

**Short-time behaviour in a dimer system**

In order to make analytical predictions about $S_{vn}(t, \alpha)$, it is useful to write it in terms of the (time-dependent) eigenvalues $\zeta_n(t, \alpha)$ of the density matrices $\rho_n(t)$:

$$S_{vn}(t, \alpha) = \sum_n \zeta_n(t, \alpha) \ln \zeta_n(t, \alpha).$$

(4.21)

These eigenvalues can be obtained after a solution of the master equation, Eq. (4.17), has been found.

Now consider a dimer system, i.e. a network consisting of two nodes that are connected to each other. The dimer can then be viewed as a small linear chain that consists of only two nodes. The Hamiltonian $H_{dimer}$ of the dimer is given by (see also Sec. 3.2.2):

$$H_{dimer} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}.$$

(4.22)

I have computed the solution to the QSW master equation, Eq. (4.17), corresponding to the Hamiltonian above, by using Mathematica. It takes the
following form:

\[
\langle 1|\rho_\alpha(t)|1 \rangle = \frac{1}{2} \left[ 1 + \frac{f}{2\nu} \exp\left( -\frac{1}{2} \alpha(3 + \lambda)t \right) \cosh(\nu t) \right] \\
\langle 1|\rho_\alpha(t)|2 \rangle = \frac{2i(1-\alpha)}{\nu} \exp\left( -\frac{1}{2} \alpha(3 + \lambda)t \right) \sinh(\nu t), \quad (4.23)
\]

where

\[
\nu = \sqrt{(4 + \alpha(\lambda - 5))(-4 + \alpha(\lambda + 3))} \\
f = \alpha(1-\lambda) + \nu. \quad (4.24)
\]

The other two components of the density matrix are given by \( \langle 2|\rho_\alpha(t)|1 \rangle = 1 - \langle 1|\rho_\alpha(t)|1 \rangle \) and \( \langle 2|\rho_\alpha(t)|1 \rangle = (\langle 1|\rho_\alpha(t)|2 \rangle)^* \).

The full expression for the eigenvalues of \( \rho_\alpha(t) \) is too large to show here, but in the short-time limit they take on a simple form. Upon expanding \( \rho_\alpha(t) \) for small \( t \), I obtain:

\[
\rho_\alpha(t) \approx \begin{pmatrix} 1 - \alpha t & -i(1-\alpha)t \\ i(1-\alpha)t & \alpha t \end{pmatrix} + \mathcal{O}(t^2). \quad (4.25)
\]

The time-dependent eigenvalues are then given by:

\[
\zeta_1(t, \alpha) \approx \alpha t + \mathcal{O}(t^2) \\
\zeta_2(t, \alpha) \approx 1 - \alpha t + \mathcal{O}(t^2). \quad (4.26)
\]

This means that for \( t \ll 1 \), the von Neumann entropy takes the following form:

\[
S_{vn}(t, \alpha) \approx \alpha t \ln \alpha t + (1-\alpha t) \ln(1-\alpha t) \\
\approx \alpha t - \alpha t \ln \alpha t. \quad (4.27)
\]

This result is similar to the one found in Ref. [58], where the authors computed the von Neumann entropy for an infinite chain, even though they have used a slightly different model than the one that is used here. They found that the entropy behaves as \( S_{vn}(t) \approx 2Dt \ln 2Dt \), where \( D \) is their dephasing rate.

This approximate form of the entropy means that initially, the entropy moves quickly from its localized initial state to a mixed state. This process also happens faster for larger values of \( \alpha \), or similarly, for stronger couplings to the environment. On the time scale where the above expression is valid, however, the excitation cannot have moved far from its initial position. This explains also why the underlying structure of the network does not appear in the functional form of \( S_{vn}(t, \alpha) \). In the next section, I will numerically explore at which time scales the entropy grows logarithmically.
4.3 Numerical study of the information dimension

Due to the complexity of the master equation of the QSW, it is hard to obtain analytical solutions for the von Neumann entropy for non-trivial networks. Therefore, in this section I will focus on solving the master equation numerically. First I will focus on the linear chain, and later I will study the Sierpinski gasket. These two examples provide two interesting cases regarding their quantum dynamics. Namely, it has been shown that for the linear chain coherent transport is more efficient than classical transport while for the Sierpinski gasket it is exactly the opposite [59, 11].

Figure 4.2: This figure shows, on a log-linear scale, the numerically computed von Neumann entropy $S_{vn}(t, \alpha)$ for a linear chain of length $N = 100$ and for various values of $\alpha$. The black dashed line illustrates the fitted logarithmic growth regime for $\alpha = 0.1$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.2.png}
\caption{This figure shows, on a log-linear scale, the numerically computed von Neumann entropy $S_{vn}(t, \alpha)$ for a linear chain of length $N = 100$ and for various values of $\alpha$. The black dashed line illustrates the fitted logarithmic growth regime for $\alpha = 0.1$.}
\end{figure}
4.3. Numerical study of the information dimension

4.3.1 Linear chain

The Hamiltonian for a linear chain of length $N$ can be written as follows [11]:

$$
H^\text{chain}_S = \sum_{n=2}^{N-1} (2\langle n \rangle \langle n | - | n - 1 \rangle \langle n | - | n + 1 \rangle \langle n |)
+ |1\rangle \langle 1 | + |N\rangle \langle N | - |2\rangle \langle 1 | - | N - 1 \rangle \langle N |.
$$

To obtain the incoherent transition rates $\gamma_{mn}$ for $m \neq n$ (see Eq. (1.43)) that appear in generator $L^\text{CTRW}[\rho_\alpha(t)]$ for the CTRW (c.f. Eq. (4.17)), I use Fermi’s golden rule. This means that the rates are given by $\gamma_{mn} = |\langle m | H^\text{chain}_0 | n \rangle|^2$ [24, 18]. From the form of the Hamiltonian it then follows that $\gamma_{mn} = \delta_{m_\pm 1,n}$ for $1 < m < N$ and that the only other nonzero rates are $\gamma_{12} = \gamma_{N,N-1} = 1$.

In the literature, the spectral dimension for a linear chain is known analytically, namely $d_s = 1$ [11]. This result also follows from Eq. (4.4), since the fractal dimension of a linear chain is equal to $d_f = 1$, while from the theory of diffusion it follows that the random walk dimension is given by its standard Euclidean value $d_w = 2$ [7]. This means that in the limit $\alpha \to 1$, the
4.3. Numerical study of the information dimension

The information dimension is given by \( \lim_{\alpha \to 1} d_I(\alpha) = d_s/2 = 1/2 \). On the other hand, for the CTQW it has been shown that the envelope of the average return probability \( \tilde{\pi}(t) \) (Eq. (1.17)) decays as \( t^{-1} \) [11]. Therefore, I expect that the information dimension for small values of \( \alpha \) approaches twice its classical value: \( \lim_{\alpha \to 0^+} d_I(\alpha) \approx 1 \).

In Fig. (4.2) I show my numerical results for the von Neumann entropy \( S_{vn}(t, \alpha) \) on a log-linear scale, for a linear chain of length \( N = 100 \). The curves that are shown there correspond to different values of \( \alpha \). For small times, the entropy grows slowly for small values of \( \alpha \) and faster for higher values of \( \alpha \). In Fig. (4.3), I show the short-time behaviour of \( S_{vn}(t, \alpha) \) in more detail. In this regime, I find a similar growth behaviour for \( \alpha t \ll 1 \) as the one that I found for the dimer. I have fitted the von Neumann entropy to the expression in Eq. (4.27) and found that it scales as:

\[
S_{vn}(t, \alpha) \approx 2 (\alpha t - \alpha t \ln \alpha t) \tag{4.29}
\]

The fitted results are shown by the black lines in Fig. (4.3). The fits have been performed up to \( \alpha t = 0.05 \). After this time the entropy transitions into the logarithmic growth regime, which I will describe next.

After an initial time \( t_I \) of the order of \( t_I \approx \mathcal{O}(1) \), the entropy changes from its initial growth towards a logarithmic growth regime. Especially for \( \alpha \geq 0.2 \), this regime is clearly visible. However, for \( \alpha = 0.1 \) this is not the case anymore. Here, this regime is estimated to lie in the time interval \( 15 \leq t \leq 35 \). The black dashed line in Fig. (4.2) illustrates this estimated region by fitting a straight line to the entropy. Since this interval is so small, there are large fitting errors when I determine the information dimension from the slope of the fitted line. I am certain that this issue can be resolved by computing the entropy for much larger chains than I do here. Namely, since the stationary value of \( S_{vn}(t, \alpha) \) is given by \( \lim_{t \to \infty} S_{vn}(t, \alpha) \approx \ln N \), taking larger values of \( N \) means that the entropy needs more time to reach its equilibrium value. This in turn implies that the logarithmic growth interval will be larger. Unfortunately, this argument also means that in order to make the logarithmic growth interval twice as large, one needs a chain of \( N' \approx \mathcal{O}(N^2) \approx \mathcal{O}(10^4) \) nodes. Currently, this is impossible to compute with the standard methods due to the memory limitations of my computer. Further investigation into this aspect will therefore have to be done in future work.

In Fig. (4.4) I show the values of the extracted information dimension for the linear chain (green). Here, I observe that \( d_I(\alpha) = 0.49 \approx d_s/2 \) for almost all values of \( \alpha \). Only close the the quantum regime, i.e. for \( \alpha \leq 0.3 \), I see an
increase in $d_I(\alpha)$. It increases towards approximately twice its classical value, namely $d_I(\alpha) \approx 1$ for small $\alpha$. Note however, that is hard to make sure that $d_I(\alpha)$ does not increase much more for even smaller values of $\alpha$. This quick change in the information dimension means that transport on a linear chain is quite sensitive to environmental interactions. Already for small couplings to the environment, the quantum speed-up is lost.

### 4.3.2 Sierpinski gasket

In this subsection, I describe the numerical results that I have computed for the Sierpinski gasket, which has been described in section 4.1. Unlike for the linear chain, it is difficult to write a general form for its corresponding Hamiltonian. For the computations in this section, I have obtained the Hamiltonian for generation $g = 5$ by using the `GraphData["Sierpinski", g]` data structure in Mathematica.

The numerical results for $S_{vn}(t, \alpha)$ for a Sierpinski gasket of generation $g = 5$ are shown in Fig. (4.5). The overall shape of the curves is similar to the ones found for the linear chain, see Fig. (4.2). Especially in the short time regime, the entropy behaves almost identical. This is in accordance with the claim of the previous section, that $S_{vn}(t, \alpha)$ only depends on $\alpha t$ when $\alpha t \ll 1,$
4.3. Numerical study of the information dimension

The fits have been performed up to $\alpha t = 0.05$. The only difference with the linear chain, is that the prefactor is now $3.8$ instead of $2$.

The biggest difference in the results of Fig. (4.5), as compared to the linear chain, is that the logarithmic growth regime is much clearer to see. This in turn, results in better fits for the information dimension $d_I(\alpha)$ for all values of $\alpha$. As an illustration, I’ve shown the fit for $\alpha = 1.0$ with the black dashed line. The results for the information dimension are shown by the red curve in Fig. (4.4). Compared to the linear chain (green curve), it changes much slower with increasing values of $\alpha$. For large values of $\alpha$, $d_I(\alpha)$ approaches the classical value $d_s/2$, while for small values of $\alpha$, for example for $\alpha = 0.1$, it approaches $d_I(0.1) = 1.412 \approx d_s$. This is again approximately twice the classical value, as was also observed for the linear
4.3. Numerical study of the information dimension

Figure 4.6: This figure shows the short-time behaviour of the von Neumann entropy $S_{vn}(t, \alpha)$ for a Sierpinski gasket of generation $g = 5$, see also Fig. (4.5). The black lines show the fitted analytical results for $S_{vn}(t, \alpha)$.

Finally, in Fig. (4.7), I show the crossing regions of both Fig. (4.2) and Fig. (4.5). The first is shown in the upper panel while the latter is shown in the lower panel. The most striking difference between the two plots, is that for the linear chain, the curve with $\alpha = 0.1$ crosses all the other ones and transitions to the equilibrium state much faster. For the Sierpinski gasket, this curve crosses the curves with small values of $\alpha$ but never reaches above the curve for $\alpha = 1.0$. This might be attributed to the fact that the spectral dimension $d_s$ is larger for the Sierpinski gasket as for the linear chain. This causes the logarithmic growth regime to grow faster for all values of $\alpha$, which implies that the curve for $\alpha = 1$ increases fast enough to avoid crossing the $\alpha = 0.1$ curve before the transition to the equilibrium state.
4.4 Discussion

In this chapter, I have studied the properties of the von Neumann entropy for the QSW, both for the linear chain and for the Sierpinski triangle. In the

Figure 4.7: This figure shows the crossing regions of the von Neumann entropy $S_{vn}(t, \alpha)$ for both a linear chain with $N = 100$ nodes (top) and for a Sierpinski gasket of generation $g = 5$. 

4.4 Discussion

In this chapter, I have studied the properties of the von Neumann entropy for the QSW, both for the linear chain and for the Sierpinski triangle. In the
classical limit, the von Neumann entropy reduces to the classical Shannon information entropy. It has been shown before that the Shannon entropy has a logarithmic growth regime for many different lattices, provided that the probability distribution can be described by a stretched exponential function. The most interesting aspect of this behavior, is that the growth rate is directly related to the spectral dimension associated to the CTRW on the network. The spectral dimension is usually defined through the scaling behaviour of the return probability of the walker and is used to classify the behavior of the CTRW for various kinds of networks. Its relation to the Shannon entropy therefore provides an interesting alternative for performing this classification process.

For the case of the CTQW, it has always been difficult to classify the dynamics for different types of networks. Unlike for the CTRW, where nice scaling relations can be derived, this is difficult due to the coherent wave nature of the walker. For instance, the envelope functions of the return probabilities show a similar scaling behavior as for the CTRW, but they are difficult to determine numerically [11]. However, when studying the von Neumann entropy for the QSW, I have found that there are no oscillations present for a wide range of parameters. Therefore it is possible to classify (almost) coherent dynamics on networks by reducing the coupling to the environment and by measuring the resulting information dimension of the QSW. The information dimension for other values of $\alpha$ also provides insight into the robustness of the quantum transport against environmental noise. This could be seen for instance for the linear chain, where the information dimension decreased much faster with increasing $\alpha$ as for the Sierpinski gasket.

To verify that my results are not an artefact of the QSW model, it is possible to use the Hierarchy Equations of Motion approach to validate these results. This is a numerically exact method that allows one to compute the reduced dynamics for a given system-environment Hamiltonian [61]. When the spectral density is of Lorenzian/Ohmic form, it is possible to effectively use this method. Because it gives the complete solution for the density matrix, it is not difficult to compute the related von Neumann entropy. While testing this approach, I found a similar logarithmic growth behavior for a wide range of couplings to the environment. However, these results are still in an early stage and therefore I have not included them in this chapter. For future work, it would be interesting to connect these computations to the ones of the QSW and to try to see if the computations done in this chapter also extend to other types of networks.
Chapter 5

Energy transfer in the FMO complex

5.1 The FMO complex

Figure 5.1: Illustration of the Fenna-Matthews-Olsen monomer. The BCHls are shown in green while the protein environment is shown by the gold ribbons. The numbers inside each BCHl refer to the site-basis representation $|n\rangle$ used to model energy transfer on this complex. This figure is taken from Ref. [31].
The Fenna-Matthews-Olsen (FMO) complex is a (water-soluble) light harvesting protein found in green sulphur bacteria (see Fig. (5.1) for an illustration). These bacteria use molecular antenna structures (chromophores) to capture low intensity light, which is then converted to an excitation. This excitation is then transferred through the FMO complex to the reaction center. In this reaction center, the excitation triggers an electron transfer process, fuelling the rest of the photosynthetic cycle. This process occurs with a remarkable unexpected efficiency, especially since it happens in a highly fluctuating disordered environment and at room temperature. Namely, classical computations predicted a much lower transport efficiency for this process [31].

The two-dimensional spectroscopy experiments [62, 63] on the FMO complex performed by the Fleming group in 2007 [64] and subsequently confirmed by the Engel group in 2010 [65], demonstrated that the conventional description of energy transport, with either Redfield [66, 17] or Förster theory [67], was no longer adequate due to the intermediate to strong coupling of the protein environment to the FMO complex. This lead to great interest in finding new methods that can accurately describe energy transfer in these regimes, as for example polaron [68, 69] and variational polaron theory [70], Lindblad master equations [71, 72, 35, 51, 46, 73], modified Redfield theory [74, 75, 76] and methods using the numerically exact Hierarchy Equations of Motion [77, 78, 79, 80].

In this chapter I will use an extension of the quantum stochastic walk to model energy transfer in an FMO monomer. In particular, I will use time-dependent dephasing rates to model the possibly non-Markovian interactions with the environment. This leads to a form of the master equation that is similar to the time-convolutionless master equation, see also Ref. [18]. To describe the detailed couplings of the protein environment to the FMO complex, I use the spectral densities from Refs. [81, 82]. They have been computed from the bath autocorrelation functions, obtained by combining molecular dynamics simulations together with methods from quantum chemistry at coarse-grained time intervals. Unfortunately, it has been shown in the literature that these spectral densities do not describe the realistic values for the couplings to the environment [83, 84, 85, 86]. Instead, they overestimate them due to a false value for the distance at which different charges in the simulation can influence each other. Nonetheless, these spectral densities still lead to a good non-trivial example of a complex system that is strongly coupled to an environment and whose coupling is different for each site of the network.
Numerically exact Path Integral Monte Carlo (PIMC) simulations have also been performed for the FMO complex with these spectral densities [22]. In this numerically exact method, the Feynman-Vernon path integral representation of the open quantum system, see Ref. [87], is evaluated with the help of the Monte Carlo simulation technique. These simulations allow me to demonstrate the validity of the quantum stochastic walk in modelling energy transfer in the aforementioned regime. Additionally to this, I compute the linear absorption spectrum and compare it to the results that were obtained with semi-classical wavepacket dynamics [82]. This provides another benchmark result, since the absorption spectrum is mostly sensitive to the dynamics of the coherences.

5.2 Energy transfer in FMO monomers

5.2.1 Microscopic description

The dynamics of single excitations in FMO monomers is typically described by a tight-binding Hamiltonian with 7 localized sites, corresponding to the 7 bacteriochlorophylls (BChls) of the FMO monomer [88, 89]. The influence of the protein scaffold and solvent on the excitonic dynamics is treated, in the spirit of the Caldeira-Leggett model [90], as a collection of harmonic modes that are linearly coupled to each BChl. Previous studies showed no significant correlations between the bath induced energy fluctuations at different sites [91, 83], so I assume that each BChl is coupled to its own individual environment. The full Hamiltonian of the system can now be written as, see Eq. (1.21):

\[ H = H_S \otimes I_B + I_S \otimes H_B + H_{SB}, \]

with

\[ H_S = \sum_n \epsilon_n |n\rangle \langle n| + \sum_{m \neq n} J_{mn} |n\rangle \langle m|, \]

\[ H_B = \sum_{n, \kappa} \left( \frac{p_{n\kappa}^2}{2m_{n\kappa}} + \frac{1}{2} m_{n\kappa} \omega_{n\kappa}^2 X_{n\kappa}^2 \right), \]

\[ H_{SB} = \sum_n |n\rangle \langle n| \left( c_{n\kappa} X_{n\kappa} + \Lambda_n^{(cl)} \right). \]

The state \(|n\rangle\) corresponds to the single-excitation state of site \(n\), the parameter \(\epsilon_n\) denotes the energy gap between ground and excited state of site \(n\), and
5.2. Energy transfer in FMO monomers

\( J_{mn} \) describes the excitonic coupling between sites \( m \) and \( n \). Furthermore, \( X_{\alpha\kappa}, P_{\alpha\kappa}, m_{\alpha\kappa} \) and \( \omega_{\alpha\kappa} \) denote the position, momentum, mass and frequency of the bath oscillators, respectively. In the interaction Hamiltonian \( H_{SB} \), the constants \( c_{\alpha\kappa} \) (in units of eV/m) denote the coupling strength between site \( n \) and the bath modes. I have included the classical reorganization energies \( \Lambda^{(cl)}_n \) as a counter-term in \( H_{SB} \) to prevent further renormalization of the site energies by the environment \([90, 92, 18]\). This quantity is defined as:

\[
\Lambda^{(cl)}_n = \frac{2}{\pi} \int_{0}^{\infty} d\omega \frac{J_n(\omega)}{\omega},
\]

where \( J_n(\omega) \) (in units of 1/s) is the spectral density of the bath that is coupled to site \( n \). In terms of the system parameters, it is given by \([18]\):

\[
J_n(\omega) = \frac{\pi}{2} \sum_{\kappa} \frac{c^2_{\alpha\kappa}}{2m_{\alpha\kappa}^2 \omega_{\alpha\kappa}} \delta(\omega - \omega_{\alpha\kappa}).
\]

The precise numerical values of the different parameters entering in the expressions above were obtained from combined quantum-classical simulations for the full FMO complex including the solvent \([81, 82]\). In these references, the authors parametrized the spectral densities as a sum of (shifted) Lorentzians:

\[
J_n(\omega) = \frac{2}{\pi \hbar} \tanh(\beta \hbar \omega/2) \left[ \sum_{k=1}^{N_e} \frac{\eta_{n,k} \gamma_{n,k}}{\gamma_{n,k}^2 + \omega^2} + \sum_{k=1}^{N_o} \frac{\bar{\eta}_{n,k} \bar{\gamma}_{n,k}}{2(\bar{\gamma}_{n,k}^2 + (\omega - \bar{\omega}_{n,k})^2)} \right],
\]

with \( \beta = 1/k_B T, N_e = 2, N_o = 13 \) and \( \eta_{n,k}, \gamma_{n,k}, \bar{\eta}_{n,k}, \bar{\gamma}_{n,k} \) and \( \bar{\omega}_{n,k} \) fitting parameters from the simulations. By noting that this particular form of the spectral density leads to a bath autocorrelation function that is a sum of decaying exponentials and damped oscillations, they were able to obtain these parameters by fitting the autocorrelation function to the data from the MD trajectories.

5.2.2 Effective master equation approach

I now use the microscopic description of the FMO complex to set up a phenomenological second order time-local quantum master equation. This master equation is an extension of the QSW master equation (Eq. (1.45)), by allowing the transition rates \( \gamma_{mn} \) to be time-dependent. In doing so, I am able to reproduce the dynamics obtained from the PIMC simulations as well
5.2. Energy transfer in FMO monomers

as extending them to, in principle, arbitrary long times. Additionally, my approach also allows to obtain results for the linear absorption spectrum which are in close accordance to the results obtained by a combination of MD simulations and electronic structure calculations [82].

The spectral density of the FMO complex [81] leads to reorganization energies $\Lambda_n^{(cl)}$ of the order of $0.02 - 0.09$ eV, which are comparable to the differences in the site energies $\epsilon_n$, while the excitonic couplings $J_{mn}$ are of the order of $1$ meV. This implies that I can expect that the protein environment is relatively strongly coupled to the FMO complex and that it therefore leads to a strong damping for the population dynamics. This is also reflected by the results of the PIMC simulations [22].

I now assume that in the long-time limit, after most of the coherences in the site basis of the system have decayed, energy transfer can be described by a classical hopping process between the different sites (BChl’s) that is induced by the protein environment. This assumption is motivated by noting that in the strict singular coupling limit, i.e. the limit where the coupling to the environment is much larger than the typical energy scale for the system, the site basis becomes the correct set of pointer states for the interaction with the environment [18]. The transfer rates $k_{mn}$ have to satisfy detailed balance, ensuring a correct equilibrium state, and are assumed to follow from Fermi’s golden rule. Furthermore, the rates should also depend on the reorganization energies $\Lambda_n^{(cl)}$ and $\Lambda_m^{(cl)}$ of the baths that are coupled to the sites $n$ and $m$, reflecting the differences in the coupling strengths of the protein environment to each BChl. For high temperatures and strong coupling to the environment, it has been shown that the transfer rate between two localized states can be described by the (classical) rate stemming from Marcus’ theory of electron transport [93, 9, 76]. This leads to transfer rates $k_{mn}$ of the form [76]:

$$k_{mn} = \sqrt{\frac{\pi \beta}{\hbar^2 \Lambda_{mn}^{(cl)}}} |J_{mn}|^2 \exp \left[ -\frac{\beta (\epsilon_n - \epsilon_m + \Lambda_{mn}^{(cl)})^2}{4 \Lambda_{mn}^{(cl)}} \right],$$

(5.8)

with $\Lambda_{mn}^{(cl)} = \Lambda_m^{(cl)} + \Lambda_n^{(cl)}$.

Aside from incoherent transfer between the sites, the environment also induces a strong dephasing on each site. In the framework of the second order TCL master equation [18], these dephasing rates (in units of $1$/fs) are given by the zero-frequency Fourier transform of the bath-autocorrelation functions:

$$\lambda_n(t) = \frac{2}{\hbar} \text{Re} \int_0^t ds \int_0^\infty \frac{d\omega}{\pi} J_n(\omega) \left( \coth(\beta \hbar \omega/2) \cos \omega s - i \sin \omega s \right).$$

(5.9)
5.3. Numerical results for the energy transfer dynamics

Here, I use the spectral densities from Eq. (5.7) and calculate the frequency integral by noting that this integral is directly related to the real part of the bath autocorrelation function that is specified in Ref. [82].

The QSW master equation that describes the excitation dynamics can now be written as the following generalization of Eq. (1.45), see also Ref. [18]:

\[
\frac{d\rho_S(t)}{dt} \equiv \mathcal{L}(t)[\rho_S(t)] = -\frac{i}{\hbar}[H_S, \rho_S(t)] + \mathcal{D}_{QSW}(t)[\rho_S(t)].
\] (5.10)

For the rest of this chapter, I will neglect the Lamb shift term that usually appears in this equation [18]. The now time-dependent dissipator \(\mathcal{D}_{QSW}(t)\) of the QSW now takes the following form, according to the considerations above:

\[
\mathcal{D}_{QSW}(t)[\rho_S(t)] = \sum_{mn} \gamma_{mn}(t) \left( L_{mn} \rho_S(t) L_{mn}^\dagger - \frac{1}{2} \{ L_{mn}^\dagger L_{mn}, \rho_S(t) \} \right).
\] (5.11)

where the rates are defined by \(\gamma_{mn}(t) = \lambda_m(t)\) and \(\gamma_{mn}(t) = k_{mn}\) for \(m \neq n\).

5.3 Numerical results for the energy transfer dynamics

To validate that the QSW model described above is a reliable model for energy transfer dynamics on the FMO complex, together with the spectral densities obtained in [81, 82], I compare my numerical results to those obtained with Path Integral Monte Carlo (PIMC) simulations, as presented in Ref. [22].

5.3.1 Population dynamics

In Fig. (5.2) I show the population dynamics that are obtained by solving the TCL master equation, Eq. (5.10), for initial conditions corresponding to a localization on the sites \(|n\rangle\), i.e. \(\rho(0) = |n\rangle \langle n|\), in comparison to the corresponding numerically exact PIMC results. The dotted curves represents the latter and the solid lines represent the results from the master equation approach. Fig. (5.3) shows an extension of the results up to 1200 and 1500 fs for initial preparations in sites 1 and 6, respectively.
5.3. Numerical results for the energy transfer dynamics

Figure 5.2: Comparison of population dynamics of the 7 different sites of the FMO complex obtained from the numerically exact PIMC results (circles) with the results from the QSW approach (solid lines) for different initial conditions localized on the sites $|n\rangle$, $n = 1, \ldots, 7$. The error bars of the PIMC data are typically smaller than the symbol size.
5.3. Numerical results for the energy transfer dynamics

In general, I observe good quantitative agreement of the QSW approach with the PIMC results for all localized initial preparations and over all observed timescales. The largest deviations are observed for an initial condition localized on site 4 for which the bath has the lowest reorganization energy (0.025 eV). Also, from Fig. (5.3) I observe a good agreement in the approach to the equilibrium state, although the decay is slightly slower than predicted by the PIMC results.

Fig. (5.4) corroborates my results. Here, the excitation is initially in one of the seven eigenstates $|\psi_n\rangle$ of $H_S$. Again I find very good agreement with the PIMC results, where once more the strongest deviations occur for the initial preparation exhibiting the largest population on site 4.

5.3.2 Coherence dynamics

Aside from the population dynamics, those of the coherences provide further insight into the time scale on which coherent transfer dominates over incoherent transfer between the sites (due to the coupling with the environment). Furthermore, by knowing the time scale on which the coherences decay, I can relate the QSW model to simulations of the absorption spectra of the FMO complex [94, 95, 78, 82] (see Sec. 5.4).

In Fig. (5.5), I show the dynamics of the coherences $C_{12}(t) = \langle 1|\rho(t)|2 \rangle$ and $C_{65}(t) = \langle 6|\rho(t)|5 \rangle$, corresponding to an initial preparation in site 1 and site 6, respectively. These two initial conditions are usually assumed to be the sites on which the excitation enters the FMO complex from the baseplate.
5.3. Numerical results for the energy transfer dynamics

Figure 5.4: Same as Fig. (5.2) but taking the eigenstates $|\Psi_n\rangle$ of $H_S$ as initial conditions.
5.3. Numerical results for the energy transfer dynamics

I observe that their real parts decay on a timescale of about 100 fs, while the imaginary part of $C_{65}(t)$ decays in about 1 ps, comparable to the time scale on which population transfer takes place. Since site 1 only has a strong coupling $J_{m1}$ with site $m = 2$ (i.e. $J_{21} \gg J_{m1}$ for $m > 2$), while site 6 is only strongly coupled to sites 5 and 7, see Ref. [82], one indeed expects that the coherences for an initial excitation in site 6 survive longer. The dynamics of the other coherences (not shown) give similar results regarding the time scales on which they decay.

Finally, I remark that since there is a decay of the coherences in the site basis, it is not possible that the coherences fully decay in the exciton basis: For a coherence between the exciton states $|\psi_m\rangle$ and $|\psi_n\rangle$, one indeed finds in the limit $t \to \infty$ that:

$$
\lim_{t \to \infty} \langle \psi_m | \rho_S(t) | \psi_n \rangle = \lim_{t \to \infty} \left[ \sum_k \langle \psi_m | k \rangle \langle k | \psi_n \rangle \mathcal{P}_k(t) + \sum_{k \neq l} \langle \psi_m | k \rangle \langle l | \psi_n \rangle C_{kl}(t) \right] \\
\approx \sum_k \langle \psi_m | k \rangle \langle k | \psi_n \rangle \mathcal{P}_k^{(eq)}
$$

(5.12)

Therefore, the coherences between the exciton states approach a stationary value that is a weighted sum of the equilibrium populations in the site basis.
5.4 Linear absorption spectrum

As indicated above, the strong dephasing that is induced by the protein environment leads to a quick decay of the coherences. Hence, the dynamics of the populations is mostly insensitive to the exact behavior of these coherences. However, other observables, such as the linear absorption spectrum, are very sensitive to the short-time behavior, where the coherences are still present [9]. I now calculate the linear absorption spectrum and compare it to the absorption spectrum that has been computed with mixed quantum-classical simulations in Ref. [82].

Analytical description

The linear absorption spectrum is given by the Fourier transform of the two-time correlation function of the transition dipole moment (TDM) operator $\mathbf{\mu}$ [9]:

$$A(\omega) = \text{Re} \int_0^\infty dt \, e^{i\omega t} \langle \mathbf{\mu}(t) \cdot \mathbf{\mu}(0) \rangle,$$

where $\mathbf{\mu}(t) = e^{iH_0 t/\hbar} \mathbf{\mu} e^{-iH_0 t/\hbar}$ is the TDM operator in the interaction picture and $\mathbf{\mu} = \sum_m \mathbf{\mu}_m (|m\rangle \langle 0| + |0\rangle \langle m|)$, with $\mathbf{\mu}_m$ the TDM vector of site $m$. The two-time correlation function is evaluated in the excitonic ground state $W^0 = |0\rangle \langle 0| \otimes \rho_B$, i.e. with no excitations present.

To compute this correlation function within the QSW approach, I use the following expression [18]:

$$\langle \mathbf{\mu}(t) \cdot \mathbf{\mu}(0) \rangle = \text{tr}_S \left\{ \mathbf{\mu}(t) \cdot \mathbf{V}(t) \right\},$$

where the vector-operator $\mathbf{V}(t)$ satisfies the QSW master equation

$$\frac{d\mathbf{V}(t)}{dt} = \mathcal{L}(t)[\mathbf{V}(t)],$$

with the initial condition

$$\mathbf{V}(0) = \mathbf{\mu} \text{tr}_B \left\{ W^0 \right\} = \mathbf{\mu} |0\rangle \langle 0| = \sum_m \mathbf{\mu}_m |m\rangle \langle 0|.$$

Here $\text{tr}_S$ and $\text{tr}_B$ denote the trace over the excitonic and environmental degrees of freedom, respectively. Due to the time dependence of the dephasing rates that appear in the generator $\mathcal{L}(t)$, I cannot obtain an analytical solution for the linear absorption spectrum. However, it is possible to derive
an analytical expression for the dipole-moment autocorrelation function by noting that the dissipator $D_{QSW}(t)[\rho_S(t)]$ decouples the populations from the coherences (see also Eqs. (1.43) and (1.44)). This implies that I can write:

$$\frac{d}{dt} \vec{V}_{kl}(t) = -\frac{1}{2} \sum_{m=1}^{N} (\gamma_{mk}(t) + \gamma_{ml}(t)) \vec{V}_{kl}(t)$$

$$\equiv -\Xi_{kl}(t) \vec{V}_{kl}(t), \quad (5.17)$$

with $\vec{V}_{kl}(t) = \langle k| \vec{V}(t)|l \rangle$. By using the expression for the initial condition $\vec{V}(0)$, Eq. (5.16), I find that:

$$\vec{V}(t) = \sum_{m} \bar{\mu}_m \exp \left[ - \int_0^t ds \Xi_{m0}(s) \right] |m\rangle \langle 0| . \quad (5.18)$$

Upon inserting this solution into the expression for the dipole-moment autocorrelation function $C_{d-d}(t) = \langle \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle$, I obtain:

$$C_{d-d}(t) = \sum_{n,\alpha} \langle \psi_\alpha | n \rangle (\bar{\mu}_\alpha \cdot \bar{\mu}_n) \exp \left[ -iE_\alpha t - \int_0^t ds \Xi_{m0}(s) \right] , \quad (5.19)$$

where, to recall, $| \psi_\alpha \rangle$ are the eigenstates of $H_S$ with eigenvalues $E_\alpha$. Furthermore, $\bar{\mu}_\alpha$ is the transition dipole moment in the energy eigenstate basis, defined as follows:

$$\bar{\mu}_\alpha = \sum_{m} \bar{\mu}_m \langle m| \psi_\alpha \rangle . \quad (5.20)$$

Unfortunately, it is only possible to evaluate the half-sided Fourier transform of $C_{d-d}(t)$ analytically when the dephasing rates $\lambda_n$ are all constant. This happens for instance in the full Markovian limit, where the dephasing rates are equal to their equilibrium values, i.e. $\lambda_n = \lim_{t \to \infty} \lambda_n(t)$. For this case, the expression for the (Markovian limit of the) linear absorption spectrum $A^{(M)}(\omega)$ becomes:

$$A^{(M)}(\omega) = \sum_{n,\alpha} \langle \psi_\alpha | n \rangle (\bar{\mu}_\alpha \cdot \bar{\mu}_n) \frac{\Xi_{n0}}{(\omega - E_\alpha/\hbar)^2 + \Xi_{n0}^2} . \quad (5.21)$$

This expression is a weighted sum of Lorentzians centered at the excitonic frequencies $\omega_\alpha = E_\alpha/\hbar$. It is almost identical to the expression that one finds in standard Redfield and modified Redfield theory [9, 62]. The expression above, however, reflects the different type of population transfer rates and dephasing mechanism that I have chosen here.
5.4. Linear absorption spectrum

\[
\begin{array}{c|cccccccc}
  m & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
  \mu_{m,x} & 0.0 & -6.10 & -5.27 & 0.0 & -6.39 & 5.16 & 0.0 \\
  \mu_{m,y} & 1.86 & 1.08 & -3.04 & 2.49 & 0.0 & 2.98 & -1.14 \\
  \mu_{m,z} & 6.07 & 1.66 & -2.10 & 5.85 & -0.45 & 2.29 & 5.85 \\
  |\tilde{\mu}_m|^2 & 40.32 & 41.09 & 41.47 & 40.45 & 41.09 & 40.70 & 35.52 \\
\end{array}
\]

Table 5.1: The numerical values for the x-, y-, and z-component as well as the absolute value squared of the transition dipole moments $\tilde{\mu}_m = (\mu_{m,x}; \mu_{m,y}; \mu_{m,z})$ in units of Debye [D]. The z axis is chosen along the $C_3$-symmetry axis of the FMO complex, and the y axis is chosen to be parallel to the $N_B - N_D$ axis of BChl 1.

**Numerical results**

Upon having a good analytical description of the linear absorption spectrum in the Markovian limit, I proceed with solving it numerically for the more general case. This is done by solving Eq. (5.15) numerically and substituting it in Eq. (5.14).

The numerical values of the TDM vectors $\tilde{\mu}_m$ are obtained by combining the data from Refs. [82] and [97] together with their relative orientations with respect to the $C_3$ symmetry axis, taken from Ref. [98]. In table 5.1 I provide the computed values of the $\tilde{\mu}_m$’s.

In Fig. (5.6) I show my numerical results for the linear absorption spectrum and compare it to the computational results obtained by Olbrich *et al.* [82], see above, that utilize the same parametrization of the Hamiltonian, Eq. (5.1), but based on ensemble-averaged wave packet dynamics [99], as well as the experimental result obtained by Freiberg *et al.* [95].

I observe that both the spectra from the latter and from the theoretical approach are shifted by $-0.04$ eV and $-0.02$ eV, respectively, compared to the experimental spectrum. When overlaying those spectra such that the position of the peaks match, I observe good agreement for the overall actual line shape, even though the QSW approach lacks the detailed features of the experiment. Note that the QSW approach yields a shift from the experimental findings that is only half as large as the one presented in Ref. [82].

I have also demonstrated the effects of inhomogeneous broadening by assuming independent Gaussian static-disorder for the site-energies [62]. Namely, inhomogeneous broadening is the widening of the peak due to (structural) disorder or spatial orientations that can be different between the various
Figure 5.6: The top figure compares the linear absorption spectra, computed with the QSW master equation (solid red), mixed quantum-classical calculations [82] (dashed green) and the one obtained by experiment [95] (dotted blue). In the lower figure, all three spectra are overlaid such that the position of the peaks are shifted to the one of the experimental result.
Figure 5.7: Inhomogeneous broadening of the absorption spectrum, computed with independent Gaussian static disorder for the site-energies with a standard deviation $\sigma = 0, 6, 12$ meV and averaged over 5000 realizations. All spectra are shifted such that their peaks overlap with the experimental result.

realizations of the system in the ensemble average. On the other hand, homogeneous broadening is the broadening of the peak due to the microscopic interactions between the system and the environment. For example, in the expression for $A^{(M)}(\omega)$ in Eq. (5.21), homogeneous broadening is determined by the constants $\Xi_{\omega_0}$.

In Fig. (5.7), I show the averaged absorption spectrum over 5000 realizations for Gaussian disorder with a standard deviation $\sigma = 0, 6$ and 12 meV. These values lie in the range that is estimated from experiments [98]. Furthermore, I see that the disorder only leads to an increase of the full width at half maximum (FWHM) of the order of 1 meV. This can be understood by noting that $\sigma$ is one order of magnitude smaller than $\Lambda_n^{(cl)}$ and the differences in the sites energies, so one expects that homogeneous broadening dominates over inhomogeneous broadening.

Recently a different prefactor for the spectral density has been suggested, i.e. linearizing $\text{tanh}(\hbar \beta \omega / 2)$ by $\hbar \beta \omega / 2$ (that is, dropping the ‘standard’ approximation in favor of the ‘harmonic’ one), to obtain a more realistic way
Figure 5.8: The top figure shows the comparison of the linear absorption spectrum, computed with the spectral density in the harmonic approximation [85], to the absorption spectra obtained from experiment [95], MD simulations [82] and the spectrum that is computed with the spectral density from Ref. [82]. The lower figure shows shifted spectra such that the positions of the peak match the experimental result.
of extracting the spectral density from semi-classical simulations [85]. In this approximation, the spectral density becomes larger at higher frequencies, leading to a small effective renormalization of the transfer rates $J_{mn}$, while the other parameters stay the same [100]. Therefore I expect only small changes to the absorption spectrum when using this spectral density. In Fig. (5.8), I provide the linear absorption spectrum that is computed with this harmonic approximation for $J_0(\omega)$. I indeed observe that for small $\omega$ the absorption spectrum is practically identical to the previous results, while for large $\omega$ the peak is slightly broader (approx. 5 meV).

Furthermore, I still see only marginal inhomogeneous broadening of the spectrum, see Fig. (5.9), but only half as large as before. This can be attributed to the stronger system-environment interactions, leading to an even stronger effect of the homogeneous broadening as compared to the inhomogeneous one.
5.5 Discussion

I have presented an approach to calculate the energy transfer dynamics on molecular complexes that are strongly coupled to an external environment. My method is based on a phenomenological master equation that is motivated by the concept of a quantum stochastic walk: the coherent evolution is determined by the Frenkel-exciton Hamiltonian of the complex, while the incoherent part describes a classical hopping process between the localized states of the complex, with rates described by Marcus’s theory of electron transport, together with a (non)-Markovian time-dependent dephasing of the excitation on each site. To illustrate this method, I have applied it to energy transfer on the FMO complex at room temperature by using non-trivial spectral densities obtained from atomistic simulations [81], describing a strong coupling of the complex to its protein environment.

I have demonstrated the quantitative reliability of this TCL master equation by comparing the population dynamics to those obtained from numerically exact PIMC simulations. I find good agreement for timescales up to the picosecond range, both for the exciton initially localized on any of the sites as well as in an excitonic eigenstate. Furthermore, I have also computed the linear absorption spectrum for the FMO complex, since this provides a way to validate the dynamics of the coherences. The lineshape of the spectrum from semi-classical wavepacket dynamics is reproduced very well and I also find good agreement with the corresponding experimental result, even after including the effects of inhomogeneous broadening. Finally, I have shown that modifying the spectral density to its harmonic form, as suggested in Ref. [85], only has little effect on my results. This suggests that in the strong coupling regime, both descriptions of the spectral density lead to similar dynamics.

While the specific method presented here is tailored to the strong-coupling case, in principle an extension to regimes of weaker coupling is straightforward by applying a suitable adjustment of the transfer and dephasing rates, and possibly the set of states over which the environmentally induced random walk takes place. This would allow, for example, to accommodate more recent results regarding the calculation of spectral densities for the FMO complex [85, 86], suggesting coherent transfer dynamics, or for LH2 complexes [101].
Summary and Outlook

In this thesis I studied the properties of the Quantum Stochastic Walk for various kinds of networks and I extended its theoretical formulation to allow for sources and drains to be attached to them. In particular, in Chap. 3, I studied the transport efficiency in the form of the expected survival time for a monomer, a dimer, a trimer and topologically disordered networks.

A common feature of the EST for all these examples is that it is only marginally influenced by the strength at which the source is coupled to the network. The coupling of the network to the drain has a much larger influence on the dynamics. Another common feature is that the EST is usually larger in the coherent regime as compared to the classical case, implying that transport is often more efficient in the classical regime. This is due to the localization that occurs because of the energetic disorder in the system. The coupling to the environment destroys the effects of the localization and in turn makes the transport more efficient. When there is no energetic disorder in the system, the situation is different. For a dimer without disorder, there exists an optimal coupling to the environment for which the transport is the most efficient. This is reminiscent of the examples of environmental-assisted transport that have attracted much attention in the literature, see for instance Refs. [46, 51, 43]. Note, however, that EST only provides a rough measure for global transport efficiency of the network. Recently, more detailed measures have been proposed that allow for a better investigation of the effects of decoherence on the transport efficiency, as for example the use of flux networks in Ref. [102]. It would be interesting to apply these measures to the networks that I have studied here.

If there is a dark state present in the system, i.e. a state that has no overlap with any of the nodes that are connected to the drain, the situation is again different. Here it is possible to choose the initial state in such a way that the detrimental effects of the dark state are completely avoided. In Chap. 3, I showed how this can be realized for a special kind of trimer network. Upon using such an initial state, it followed that coherent transport
is much more efficient than in the other cases. This result shows in particular that not only the topology of the network is of importance, but also the state in which the excitation is initialized.

Another goal of this thesis was to try to get insight in the classification of both coherent and incoherent transport on networks. For the classical case, this can be done by looking at dynamical properties that arise from the structure of the underlying network. In particular, one can classify transfer processes by either the fractal dimension or the spectral dimension. The latter is a scaling exponent related to the average return probability of the walker. In Chap. 4, I extended this idea to the QSW. Instead of looking at the return probabilities, I focussed on the behavior of the von Neumann entropy. In the classical limit it reduces to the Shannon information entropy, for which it has been shown that it has a logarithmic growth regime whose slope is directly related to the spectral dimension. I showed that this behavior extends for a large range of couplings to the environment, but with a different growth rate of the logarithmic growth regime. The von Neumann entropy therefore provides a useful tool to observe the differences between coherent and incoherent transport. This could be clearly seen in the different behavior I found between the linear chain and the Sierpinski gasket. It would be of great interest to see if the von Neumann entropy shows similar characteristics for other types of networks. Numerical computations on graphical processors could help to compute the entropy for much larger networks than the ones I studied in this thesis. This is of particular importance, since the logarithmic growth regimes are hard to observe in the near coherent regime when the network has a small number of nodes.

Finally, I applied the QSW to study energy transfer in the FMO complex. This is a light-harvesting complex found in green sulphur bacteria and has received much attention in recent years. To model the energy transfer, I modified the QSW to allow for time-dependent dephasing rates. I computed these rates by using microscopic parameters that were obtained by MD simulations. This allowed me to reproduce the numerically exact PIMC results that were made by L. Mühlbacher in Ref. [22]. Furthermore, I have been able to qualitatively reproduce the linear absorption spectra that were obtained in the MD simulations. This means that the QSW model could be a good tool to model complex energy transfer processes in molecular systems which have a strong coupling to the environment. However, more investigation has to be done to see for which microscopic models and parameters it is possible to model the dynamics with the QSW. This could also provide insight into the possibility of deriving the QSW master equation from a microscopic
Hamiltonian.

To conclude: I have found in this work that the QSW is an interesting model for describing both coherent and incoherent transport processes on networks and that it is able to demonstrate many interesting global physical properties related to various kinds of networks. Although it is only a phenomenological model, it can still be used to qualitatively understand energy transfer processes in molecular complexes. Future studies of the QSW for different kinds of networks and for different microscopic systems can then provide more insight into the physics of transport on networks.
Bibliography


