

EBERHARD KARLS UNIVERSITÄT TÜBINGEN
&
UNIVERSIDAD DE GRANADA

MASTER THESIS

Master thesis

Author:
Leopold BODAMER

Supervisor:
Prof. Dr. Daniel Manzano
Diosdado

*A thesis submitted in fulfillment of the requirements
for the degree of Master of Science*

in

Theoretical Atomic Physics and Synthetic Quantum Systems
Institut für Theoretische Physik

March 26, 2025

Contents

Contents	iii
1 Introduction	1
1.1 Coherence and Excitation Transport	1
1.2 Motivation	2
1.3 Bath Correlators and Transition Rates	3
1.3.1 Bath Correlator	3
2 Chapter Title Here	7
2.1 Derivation of the Lindblad equation from microscopic dynamics	7
A Appendix Title Here	9

Chapter 1

Introduction

1.1 Coherence and Excitation Transport

In this chapter, we aim to explain the phenomena of long coherences (lifetimes) and the excitation transport of light on a microtubule. The proposed model takes the following approach:

- The microtubule is modeled as a cylindrical structure consisting of nodes. Each node represents an atom, which is modeled as a two-level system. The number of atoms, N_{atoms} , is determined by the number of chains (n_{chains}) and the number of rings (n_{rings}), assuming fixed positions for these nodes.
- The system is restricted to a single excitation.
- A time-dependent coupling to an electric field is proposed, which may be either classical or quantum in nature. This coupling is intended to facilitate spectroscopy.
- Two types of Lindblad operators are introduced to model dissipation processes. Specifically:
 1. Spontaneous decay
 2. Dephasing

The Lindblad operators introduced to model the spontaneous decay and dephasing processes for each individual atom are defined as follows:

$$C_{\text{decay}}^{(i)} = \sqrt{\gamma_0} \sigma_-^{(i)}, \quad (1.1)$$

$$C_{\text{dephase}}^{(i)} = \sqrt{\gamma_\phi} \sigma_z^{(i)}, \quad (1.2)$$

where:

- $C_{\text{decay}}^{(i)}$ describes the spontaneous decay of the i -th atom, with a rate given by γ_0 .
- $C_{\text{dephase}}^{(i)}$ describes the dephasing of the i -th atom, with a rate given by γ_ϕ .
- $\sigma_-^{(i)}$ is the lowering operator for the i -th atom, and $\sigma_z^{(i)}$ is the Pauli z -operator for the i -th atom.

1.2 Motivation

It is widely assumed that one of the crucial tasks currently facing quantum theorists is to understand and characterize the behaviour of realistic quantum systems. In any experiment, a quantum system is subject to noise and decoherence due to the unavoidable interaction with its surroundings. The theory of open quantum systems aims at developing a general framework to analyze the dynamical behaviour of systems that, as a result of their coupling with environmental degrees of freedom, will no longer evolve unitarily. [1]

2DES> [2], [3], [4]

NONlinear Optics> [5], [6]

Spectroscopy investigates the interaction between matter and electromagnetic radiation, offering a means to analyze composition and structure. Central to this analysis is the understanding of how molecules respond to specific frequencies of light, revealing information about their energy levels and bonding. Key concepts include wavelength (λ), wavenumber ($\bar{\nu}$), and frequency (ν). Wavelength, the distance between successive wave crests, is typically measured in nanometers or micrometers. Wavenumber, expressed in inverse centimeters (cm^{-1}), represents the number of waves per unit distance and is directly proportional to energy, defined as $\bar{\nu} = 1/\lambda$ (where λ is in cm). Frequency, the number of wave cycles per second, is measured in Hertz (Hz), and the angular frequency (ω) is related to frequency by $\omega = 2\pi\nu$. The relationship between angular frequency and wavenumber is given by $\omega = 2\pi c\bar{\nu}$, where c is the speed of light.

Next, I converted all units into femtoseconds (fs^{-1}), which is commonly used in time-domain spectroscopy.

Spectrometers are instruments designed to measure the intensity of light as a function of wavelength or frequency.

Different types of spectrometers are employed for various regions of the electromagnetic spectrum. Notably, UV-Vis spectrometers analyze absorption and transmission of ultraviolet and visible light, while infrared (IR) spectrometers measure the absorption of infrared light, providing insights into molecular vibrations. Nuclear Magnetic Resonance (NMR) spectrometers probe the magnetic properties of atomic nuclei, revealing molecular structure.

1.3 Bath Correlators and Transition Rates

The quantum mechanical state of a bosonic bath in thermal equilibrium at temperature T is given by the density matrix:

$$\rho = \frac{1}{Z} e^{-\beta H}, \quad Z = \text{Tr} [e^{-\beta H}]$$

And the expectation value of an operator A in a system S is given by:

$$\langle A \rangle_T = \text{Tr}_S [\rho_S A] = \frac{1}{Z} \sum_n e^{-\beta E_n} A_{nn},$$

where $|n\rangle$ are number states. The inverse temperature β is defined as:

$$\beta = \frac{1}{k_B T}$$

1.3.1 Bath Correlator

The bath correlator is given by:

$$C(\tau) = \langle B(\tau) B(0) \rangle$$

where the bath operator B is defined as:

$$B = \sum_{n=1}^{\infty} c_n x_n$$

and the bath operator in terms of creation and annihilation operators is:

$$B(0) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2m_n \omega_n}} (b_n + b_n^\dagger),$$

$$B(\tau) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2m_n \omega_n}} (b_n e^{-i\omega_n \tau} + b_n^\dagger e^{i\omega_n \tau}).$$

Substituting $B(\tau)$ and $B(0)$ into the bath correlator expression:

$$C(\tau) = \left\langle \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2m_n \omega_n}} (b_n e^{-i\omega_n \tau} + b_n^\dagger e^{i\omega_n \tau}) \sum_{m=1}^{\infty} c_m \sqrt{\frac{1}{2m_m \omega_m}} (b_m + b_m^\dagger) \right\rangle.$$

Applying the thermal expectation values:

$$\langle b_n b_m^\dagger \rangle = \delta_{nm} (n_n + 1), \quad \langle b_n^\dagger b_m \rangle = \delta_{nm} n_n,$$

where n_n is the Bose-Einstein distribution:

$$n_n = \frac{1}{e^{\beta \omega_n} - 1}.$$

We get:

$$C(\tau) = \sum_{n=1}^{\infty} \frac{c_n^2}{2m_n \omega_n} [(n_n + 1) e^{-i\omega_n \tau} + n_n e^{i\omega_n \tau}].$$

Next, we express the correlation in terms of the spectral density $J(\omega)$, which is defined as:

$$J(\omega) = \pi \sum_{n=1}^{\infty} \frac{c_n^2}{2m_n\omega_n} \delta(\omega - \omega_n).$$

Thus, the bath correlator becomes:

$$C(\tau) = \int_0^{\infty} d\omega \frac{J(\omega)}{\pi} [(n(\omega) + 1)e^{-i\omega\tau} + n(\omega)e^{i\omega\tau}].$$

Rearranging the terms, we get:

$$C(\tau) = \int_0^{\infty} d\omega \frac{J(\omega)}{\pi} \left[\coth\left(\frac{\beta\omega}{2}\right) \cos(\omega\tau) - i \sin(\omega\tau) \right].$$

This is the desired result:

$$C(\tau) = \int_0^{\infty} d\omega \frac{J(\omega)}{\pi} \left(\coth\left(\frac{\omega}{2}\right) \cos(\omega\tau) - i \sin(\omega\tau) \right)$$

Conversion from Discrete Sum to Continuous Spectral Density

In the theory of open quantum systems, one often moves from a discrete description of the bath to a continuous one. This is summarized by the transformation:

$$\sum_{j=1}^M g_j^2 \delta(\omega - \omega_j) \longrightarrow J(\omega).$$

1. Discrete Modes

The bath is initially described as a set of M harmonic oscillators:

- Each oscillator has frequency ω_j .
- Each oscillator couples to the system with coupling constant g_j .

The spectral contribution of each oscillator is:

$$\sum_{j=1}^M g_j^2 \delta(\omega - \omega_j).$$

2. Density of States

As $M \rightarrow \infty$ and the frequencies $\{\omega_j\}$ become dense, replace the sum by an integral:

$$\sum_{j=1}^M \longrightarrow \int d\omega' \rho(\omega'),$$

where $\rho(\omega')$ is the density of states, indicating how many modes lie near frequency ω' .

3. Frequency-Dependent Coupling

In the continuum limit, the coupling g_j becomes a function of frequency, $g(\omega')$. Hence:

$$g_j^2 \longrightarrow g(\omega')^2.$$

4. Form of $J(\omega)$

Putting these together, one obtains

$$\sum_{j=1}^M g_j^2 \delta(\omega - \omega_j) \longrightarrow \int_0^\infty d\omega' \rho(\omega') g(\omega')^2 \delta(\omega - \omega').$$

Using the sifting property of the delta function, this becomes

$$J(\omega) = \rho(\omega) g(\omega)^2.$$

5. Ohmic Spectral Density with Exponential Cutoff

Source: Ulrich Weiss chapter 7.3: (*my interpretation: The Redfield equation is influenced by classical phenomenological models of dissipation*) In the strict Ohmic case, damping is frequency-independent. $\gamma(\omega) = \gamma$. In this case the spectral density is given by::

$$J(\omega) \propto \gamma \omega \tag{1.3}$$

for all frequencies ω , which implies memoryless friction. However, in reality this idealization can't hold because every spectral density falls to 0 for $\omega \rightarrow \infty$. Analogy to classical resistor, where the dissipation is proportional to the current.

A commonly used form in open quantum system models is the Ohmic spectral density with an exponential cutoff:

$$J(\omega) = \alpha \omega e^{-\omega/\omega_c},$$

where:

- α is a dimensionless coupling constant,
- ω_c is a high frequency cutoff.

“Ohmic” means $J(\omega) \propto \omega$ for small ω , and the exponential cutoff ensures convergence at large ω .

Chapter 2

Chapter Title Here

2.1 Derivation of the Lindblad equation from microscopic dynamics

The most common derivation of the Lindblad master equation is based on open quantum theory. The Lindblad equation is then an effective motion equation for a subsystem that belongs to a more complicated system. This derivation can be found in several textbooks such as Breuer and Petruccione [**breuer_theory_2009**] A total system belonging to a Hilbert space \mathcal{H}_T is divided into our system of interest, belonging to a Hilbert space \mathcal{H}_S , and the environment living in \mathcal{H}_E .

The evolution of the total system is given by the von Neumann equation,

$$\dot{\rho}_T(t) = -i[H_T, \rho_T(t)]. \quad (2.1)$$

As we are interested in the dynamics of the system without the environment, we trace over the environment degrees of freedom to obtain the reduced density matrix of the system $\rho(t) = \text{Tr}_E[\rho_T]$. The total Hamiltonian can be separated as

Step 1: Interaction picture

$$H_T = H_S \otimes \mathbb{I}_E + \mathbb{I}_S \otimes H_E + \alpha H_I, \quad (2.2)$$

where $H_S \in \mathcal{H}_S$, $H_E \in \mathcal{H}_E$, and $H_I \in \mathcal{H}_T$ represents the interaction between the system and the environment with coupling strength α . The interaction term is typically decomposed as

$$H_I = \sum_i S_i \otimes E_i, \quad (2.3)$$

where $S_i \in \mathcal{B}(\mathcal{H}_S)$ and $E_i \in \mathcal{B}(\mathcal{H}_E)$.

To describe the system dynamics, we move to the interaction picture where the operators evolve with respect to $H_S + H_E$,

$$\hat{O}(t) = e^{i(H_S+H_E)t} O e^{-i(H_S+H_E)t}. \quad (2.4)$$

The time evolution in the interaction picture is given by

$$\dot{\hat{\rho}}_T(t) = -i\alpha[\hat{H}_I(t), \hat{\rho}_T(t)], \quad (2.5)$$

Step 2: Expand which can be formally integrated as

$$\hat{\rho}_T(t) = \hat{\rho}_T(0) - i\alpha \int_0^t ds [\hat{H}_I(s), \hat{\rho}_T(s)]. \quad (2.6)$$

$$\dot{\hat{\rho}}_T(t) = -i\alpha [\hat{H}_I(t), \hat{\rho}_T(0)] - \alpha^2 \int_0^t [\hat{H}_I(t), [\hat{H}_I(t'), \hat{\rho}_T(t')]] dt'. \quad (2.7)$$

$$\int_t^{t'} ds \hat{\rho}_T(s) = -i \int_t^{t'} [\hat{H}_I(s), \hat{\rho}_T(s)] ds, \quad (2.8)$$

$$\hat{\rho}_T(t') - \hat{\rho}_T(t) = -i\alpha \int_t^{t'} [\hat{H}_I(s), \hat{\rho}_T(s)] ds. \quad (2.9)$$

$$\dot{\hat{\rho}}_T(t) = -i\alpha [\hat{H}_I(t), \hat{\rho}_T(0)] - \alpha^2 \int_0^t [\hat{H}_I(t), [\hat{H}_I(t'), \hat{\rho}_T(t')]] + \mathcal{O}(\alpha^3). \quad (2.10)$$

Step 3: Partial trace

$$\dot{\rho}_S(t) = -i\alpha [\hat{H}_I(t), \hat{\rho}_T(0)] - \alpha^2 \int_0^t ds \text{Tr}_E [\hat{H}_I(t), [\hat{H}_I(s), \rho_S(t) \otimes \rho_E]]. \quad (2.11)$$

Approximation

$$\hat{\rho}_T(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_E(0) \quad (2.12)$$

using eq.

$$\sum_i \text{Tr}_E [S_i \otimes E_i, \hat{\rho}_S(0) \otimes \hat{\rho}_E(0)] = \sum_i (S_i \hat{\rho}_S(0) - \hat{\rho}_S(0) S_i) \cdot \text{Tr}_E [E_i \hat{\rho}_E(0)] \quad (2.13)$$

Argue that

$$\langle E_i \rangle_E = \text{Tr}_E [E_i \hat{\rho}_E(0)] \quad (2.14)$$

with new Hamiltonian ...

$$\hat{H}'_S = \hat{H}_S + \sum_i S_i \otimes (E_i - \langle E_i \rangle_E) \quad (2.15)$$

TODO FINISH this derivation

Appendix A

Appendix Title Here

Write your Appendix content here.

Bibliography

- [1] Ángel Rivas et al. *Markovian master equations: a critical study* *New Journal of Physics* **12** p. 113032 (2010)
- [2] Jannis Krumland et al. *Two-dimensional electronic spectroscopy from first principles*. Oct. 27, 2023. DOI: [10.48550/arXiv.2308.09062](https://doi.org/10.48550/arXiv.2308.09062). arXiv: [2308.09062](https://arxiv.org/abs/2308.09062)[cond-mat]. URL: <http://arxiv.org/abs/2308.09062> (visited on 02/07/2025).
- [3] Javier Segarra-Martí et al. *Towards Accurate Simulation of Two-Dimensional Electronic Spectroscopy* *Topics in Current Chemistry* **376** p. 24 (2018)
- [4] Haoran Sun et al. *Two-dimensional spectroscopy of open quantum systems*. Dec. 14, 2024. DOI: [10.48550/arXiv.2412.10931](https://doi.org/10.48550/arXiv.2412.10931). arXiv: [2412.10931](https://arxiv.org/abs/2412.10931)[cond-mat]. URL: <http://arxiv.org/abs/2412.10931> (visited on 02/11/2025).
- [5] Peter Hamm *Principles of nonlinear optical spectroscopy: a practical approach* ()
- [6] Shaul Mukamel. *Principles of Nonlinear Optical Spectroscopy*. New York: Oxford University Press, 1995. 543 pp. ISBN: 0-19-509278-3.