Eberhard Karls Universität Tübingen
&
Universidad de Granada

Master Thesis

Master thesis

Author:
Leopold Bodamer

Supervisor:
Prof. Dr. Daniel Manzano
Diosdado

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Contents

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:

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

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

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.

Chapter 2

Derivation of the Redfield Equation

2.1 Derivation 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:

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

where $\rho_T(t)$ is the density matrix of the total system, and H_T is the total Hamiltonian.

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 $\rho(t) = \mathrm{Tr}_E[\rho_T]$. The total Hamiltonian can be separated as:

$$H_T = H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E + \alpha H_I, \tag{2.2}$$

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:

$$H_I = \sum_i S_i \otimes E_i, \tag{2.3}$$

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

2.1.1 Interaction Picture

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

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

The time evolution in the interaction picture is given by:

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

which can be formally integrated as:

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

Expanding to second order in α, we obtain:

$$\dot{\rho}_T(t) = -i\alpha\left[\hat{H}_I(t), \hat{\rho}_T(0)\right] - \alpha^2 \int_0^t \left[\hat{H}_I(t), \left[\hat{H}_I(t'), \hat{\rho}_T(t')\right]\right] dt' + \mathcal{O}(\alpha^3). \qquad (2.7)$$

2.1.2   Partial Trace and Approximation

Taking the partial trace over the environment, we obtain:

$$\dot{\rho}_S(t) = -i\alpha[\hat{H}_I(t), \hat{\rho}_T(0)] - \alpha^2 \int_0^t ds\,\mathrm{Tr}_E\left[\hat{H}_I(t), [\hat{H}_I(s), \rho_S(t) \otimes \rho_E]\right]. \qquad (2.8)$$

Assuming an initial product state:

$$\hat{\rho}_T(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_E(0), \qquad (2.9)$$

and using the relation:

$$\sum_i \mathrm{Tr}_E\left[S_i \otimes E_i, \hat{\rho}_S(0) \otimes \hat{\rho}_E(0)\right] = \sum_i \left(S_i\hat{\rho}_S(0) - \hat{\rho}_S(0)S_i\right) \cdot \mathrm{Tr}_E\left[E_i\hat{\rho}_E(0)\right], \qquad (2.10)$$

we define:

$$\langle E_i\rangle_0 \equiv \mathrm{Tr}_E\left[E_i\hat{\rho}_E(0)\right]. \qquad (2.11)$$

The total Hamiltonian can then be rewritten as:

$$H_T = H_S' + H_E + \alpha H_I', \qquad (2.12)$$

where:

$$H_S' = H_S + \sum_i S_i \otimes (E_i - \langle E_i\rangle_0), \qquad (2.13)$$

and:

$$H_I' = \sum_i S_i \otimes (E_i - \langle E_i\rangle_0). \qquad (2.14)$$

2.1.3   Final Expression

Defining $s' = t - s$, we rewrite the second-order term as:

$$\dot{\rho}_S(t) = \alpha^2 \int_0^t ds\,\mathrm{Tr}_E\bigg\{\hat{H}_I(t)\left[\hat{H}_I(t-s)\hat{\rho}_T(t) - \hat{\rho}_T(t)\hat{H}_I(t-s)\right]$$
$$- \left[\hat{H}_I(t-s)\hat{\rho}_T(t) - \hat{\rho}_T(t)\hat{H}_I(t-s)\right]\hat{H}_I(t)\bigg\}. \qquad (2.15)$$

Assuming:

$$\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(t), \qquad (2.16)$$

and expanding Eq. (2.15), we obtain:

$$\dot{\rho}_T(t) = \alpha^2 \int_0^t ds\bigg\{\mathrm{Tr}_E\left[\hat{H}_I(t)\hat{H}_I(t-s)\hat{\rho}_T(t)\right] - \mathrm{Tr}_E\left[\hat{H}_I(t)\hat{\rho}_T(t)\hat{H}_I(t-s)\right] - $$
$$\mathrm{Tr}_E\left[\hat{H}_I(t-s)\hat{\rho}_T(t)\hat{H}_I(t)\right] + \mathrm{Tr}_E\left[\hat{\rho}_T(t)\hat{H}_I(t-s)\hat{H}_I(t)\right]\bigg\}. \qquad (2.17)$$

Now, inserting the interaction Hamiltonian by tracking the operators at time $t - s$ with i' and at t with i, we have:

$$\dot{\rho}_T(t) = \alpha^2 \sum_{i,i'} \int_0^t ds \Big\{ \mathrm{Tr}_E \big[\hat{S}_i(t) \hat{S}_{i'}(t - s) \hat{\rho}_S(t) \otimes \hat{E}_i(t) \hat{E}_{i'}(t - s) \hat{\rho}_E(t) \big] -$$

$$\mathrm{Tr}_E \big[\hat{S}_i(t) \hat{\rho}_S(t) \hat{S}_{i'}(t - s) \otimes \hat{E}_i(t) \hat{\rho}_E(t) \hat{E}_{i'}(t - s) \big] -$$

$$\mathrm{Tr}_E \big[\hat{S}_{i'}(t - s) \hat{\rho}_S(t) \hat{S}_i(t) \otimes \hat{E}_{i'}(t - s) \hat{\rho}_E(t) \hat{E}_i(t) \big] +$$

$$\mathrm{Tr}_E \big[\hat{\rho}_S(t) \hat{S}_{i'}(t - s) \hat{S}_i(t) \otimes \hat{\rho}_E(t) \hat{E}_{i'}(t - s) \hat{E}_i(t) \big] \Big\}. \tag{2.18}$$

Since the trace only acts on the environment, the system operators can be taken out of the trace, and we define the correlation functions:

$$C_{ij}(t - s) = \mathrm{Tr}_E \big[\hat{E}_i(t) \hat{E}_{i'}(t - s) \hat{\rho}_E(t) \big], \tag{2.19}$$

such that:

$$\dot{\rho}_T(t) = \alpha^2 \sum_{i,i'} \int_0^t ds \Big\{ C_{ij}(t - s) \big[\hat{S}_i(t), \hat{S}_{i'}(t - s) \hat{\rho}_S(t) \big] + \mathrm{H.c.} \Big\}. \tag{2.20}$$

Chapter 3

Bath Correlation functions

3.0.1 Bath Correlator

The general task of this chapter is to calculate the bath correlator, which is defined as:

$$C(\tau) = \langle B(\tau)B(0)\rangle, \tag{3.1}$$

It is often also called two point correlation function and can bee seen as measuring the operator B at two different times in the bath. The bath operator B will be specified later.

3.1 Usefull tools

3.1.1 Infinite Geometric Series

An infinite geometric series is a series of the form:

$$S = a + ar + ar^2 + ar^3 + \cdots = \sum_{n=0}^{\infty} ar^n, \tag{3.2}$$

where a is the first term and r is the common ratio. If $|r| < 1$, the sum converges to:

$$S = \frac{a}{1-r}. \tag{3.3}$$

Derivation of the Eq. (3.3) with respect to r returns another usefull series, to be used in the subsequent calculations:

$$\sum_{n=0}^{\infty} nr^n = \frac{r}{(1-r)^2}, \quad \text{for } |r| < 1, \tag{3.4}$$

3.1.2 Trace

If we have a bipartite system $A \otimes B$, the reduced density matrix of system A is obtained by tracing out system B:

$$\rho_A = \text{Tr}_B[\rho_{AB}]. \tag{3.5}$$

If one is interested in the expectation value of an operator A in a system S, this can be calculated with the trace:

$$\langle A \rangle_S = \text{Tr}_S[\rho_S A] = \frac{1}{Z} \sum_n e^{-\beta E_n} A_{nn}, \tag{3.6}$$

where the inverse temperature β is defined as:

$$\beta = \frac{1}{k_B T}. \tag{3.7}$$

3.2   Harmonic Oscillators

A bosonic bath is modeled by an infinitely big set of harmonic oscillators, which we assume to be in thermal equilibrium. For such a system the thermal state is described by the Gibbs distribution:

$$\rho = \frac{e^{-\beta H}}{Z}, \quad H = \sum_k \hbar \omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right), \tag{3.8}$$

3.2.1   Single Mode

For a single mode k harmonic oscillator $H = \hbar \omega_k a_k^\dagger a_k$ in thermal equilibrium at temperature T, the density matrix is given by:

$$\rho = \frac{e^{-\beta \hbar \omega_k a_k^\dagger a_k}}{Z}, \tag{3.9}$$

where ω_k is the constant frequency of the mode k. The partition function can be calculated by the geometric series:

$$Z = \mathrm{Tr}\left[e^{-\beta H} \right] = \sum_{m=0}^{\infty} \langle m | e^{-\beta \hbar \omega_k a_k^\dagger a_k} | m \rangle = \sum_{k=0}^{\infty} \langle m | m \rangle \delta_{km} e^{-\beta \hbar \omega_k k} = \frac{1}{1 - e^{-\beta \hbar \omega_k}}. \tag{3.10}$$

where $|n\rangle$ are number states. Using this, the expectation value of the number operator can be calculated:

$$n_k = \langle a_k^\dagger a_k \rangle_{\mathrm{th}} = \mathrm{Tr}\left[a_k^\dagger a_k \frac{e^{-\beta H}}{Z} \right] \tag{3.11}$$

$$= \frac{\mathrm{Tr}\left[a_k^\dagger a_k e^{-\beta \hbar \omega_k a_k^\dagger a_k} \right]}{Z} \tag{3.12}$$

$$= \frac{\sum_{m=0}^{\infty} \langle m | a_k^\dagger a_k e^{-\beta \hbar \omega_k a_k^\dagger a_k} | m \rangle}{\frac{1}{1 - e^{-\beta \hbar \omega_k}}} \tag{3.13}$$

$$= \frac{1}{e^{\beta \hbar \omega_k} - 1}. \tag{3.14}$$

where we have used Eq. (3.4) in the last step.

The partition function for the infinite set then generalizes to a product:

$$Z = \prod_k \frac{e^{-\beta \hbar \omega_k / 2}}{1 - e^{-\beta \hbar \omega_k}}. \tag{3.15}$$

3.3 Bath Correlators

Now we turn to calculating the Correlator. The bath operator B is:

$$B = \sum_{n=1}^{\infty} c_n x_n. \tag{3.16}$$

With this definition note, that in sec. 2.1 the interaction hamiltonian reduces, such that only one bath correlator $C(\tau) \equiv C_{ii}(\tau)$ in Eq. (2.19) remains.

Expressing B in terms of creation and annihilation operators:

$$B(0) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2m_n\omega_n}}(b_n + b_n^\dagger), \tag{3.17}$$

$$B(\tau) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2m_n\omega_n}}\left(b_n e^{-i\omega_n\tau} + b_n^\dagger e^{i\omega_n\tau}\right). \tag{3.18}$$

Substituting $B(\tau)$ and $B(0)$ into Eq. (3.1):

$$C(\tau) = \left\langle \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2m_n\omega_n}}(b_n e^{-i\omega_n\tau} + b_n^\dagger e^{i\omega_n\tau}) \sum_{m=1}^{\infty} c_m \sqrt{\frac{1}{2m_m\omega_m}}(b_m + b_m^\dagger) \right\rangle. \tag{3.19}$$

Using the thermal expectation values:

$$\langle b_n b_m^\dagger \rangle = \delta_{nm}(n_n + 1), \quad \langle b_n^\dagger b_m \rangle = \delta_{nm} n_n, \tag{3.20}$$

where n_n is the Bose-Einstein distribution:

$$n_n = \frac{1}{e^{\beta\omega_n} - 1}. \tag{3.21}$$

We obtain:

$$C(\tau) = \sum_{n=1}^{\infty} \frac{c_n^2}{2m_n\omega_n} \left[(n_n + 1)e^{-i\omega_n\tau} + n_n e^{i\omega_n\tau}\right]. \tag{3.22}$$

3.3.1 Spectral Density Representation

Expressing $C(\tau)$ in terms of the spectral density $J(\omega)$, defined as:

$$J(\omega) = \pi \sum_{n=1}^{\infty} \frac{c_n^2}{2m_n\omega_n}\delta(\omega - \omega_n) = \sum_{n=1}^{\infty} g_j^2\,\delta(\omega - \omega_j), \tag{3.23}$$

Where the bath is described as a set of harmonic oscillators. Each oscillator has frequency ω_n and couples via a unique coupling constant g_n to the system.

With this the bath correlator becomes:

$$C(\tau) = \int_0^{\infty} d\omega \frac{J(\omega)}{\pi} \left[(n(\omega) + 1)e^{-i\omega\tau} + n(\omega)e^{i\omega\tau}\right]. \tag{3.24}$$

3.3.2   How to get from discrete to continuum

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

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

where $\rho(\omega')$ is the density of states, indicating how many modes lie near frequency ω'. In this continuum limit, the coupling g_j generally becomes a function of frequency, $g(\omega')$:

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

Putting these together, one obtains

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

Using the sifting property of the delta function, this becomes

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

For this continuum limit, the bath correlator becomes:

$$C(\tau) = \int_0^{\infty} d\omega\, \frac{J(\omega)}{\pi} \left[\coth\left(\frac{\beta\omega}{2}\right) \cos(\omega\tau) - i\sin(\omega\tau)\right]. \tag{3.25}$$

This is the final result for the bath correlator.

3.3.3   Ohmic Spectral Density

A commonly used parametrization of the spectral density is made with an exponential cutoff:

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

to ensure that the Correlation function decays in time domain. this function is called (sub-/super-/) Ohmic for the values of $s(< / > / =)1$ respectively. "Ohmic" means $J(\omega) \propto \omega$ for small ω The correspondance is drawn to electric capacitor, where the damping is proportion to the velocity. In the expression

- η is a dimensionless coupling constant,

- ω_c is the cutoff frequency.

Appendix A

Appendix Title Here

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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`. arXiv: `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`. arXiv: `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.