

# Open Quantum Systems Theory behind Quantarhei Package

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In this document, we summarize the theory of open quantum systems as it is implemented in the Quantarhei package. Before it grows into a self-contained text, the following books should be consulted to get a full picture: Volkhard May and Oliver Kühn, *Charge and Energy Transfer in Molecular Systems*, Wiley-VCH, Berlin, 2000 (and later editions), Shaul Mukamel, *Principles of Nonlinear Spectroscopy*, Oxford University Press, Oxford, 1995 and Leonas Valkunas, Darius Abramavicius and Tomáš Mančal, *Molecular Excitation Dynamics and Relaxation*, Wiley-VCH, Weinheim, 2013.

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# Chapter 1

## Introduction

Quantap*ε*l deals with the dynamics and spectroscopy of molecular systems. This is said mainly to stress that we are far away from the part of physics usually known as solid state physics or solid state theory. There is no prejudice or personal liking behind this. It is to say that there are huge differences in theoretical approaches to a problem of regular solid and small molecular aggregates. Many concepts discussed here do apply in solid state problems and many do not. It is a huge mistake to think that concepts that bear the same name are automatically transferable across the theoretical domains such as chemical physics and solid state physics.

We do not explain quantum mechanics itself here.

## Chapter 2

# Closed Quantum Systems

Quantum theory is build upon a concept of a closed quantum system. This is a necessary idealization which we need for a start. It would be, however, better to completely forget it once the concepts of quantum theory become somewhat more familiar. Later in this text, we will try to explain why.

We describe those physical properties of a molecular (or atomic) system that are important for its dynamics by the so-called Hamiltonian (or energy) operator  $\hat{H}$ . The state of the system is described by a state vector  $|\psi(t)\rangle$  which can be time dependent. All operators, not just the Hamiltonian can act of the state vector and change it

$$|\phi\rangle = \hat{H}|\psi\rangle. \quad (2.1)$$

Eq. (2.1) is not meant to descibe any physics. It is not like taking a tool and acting with it on a physical system. We mean acting in a matematical sense. We have a vector  $|\psi\rangle$ , and when we apply an operator  $\hat{H}$  to it, we get a different vector.

The signature of the two vectors being different is the fact that their scalar product, once they are normalized, is not one. For all state vectors we assume

$$\langle\psi(t)|\psi(t)\rangle = 1, \quad (2.2)$$

i.e. we assume that they are normalized to one. In general, if  $|\psi\rangle$  and  $|\phi\rangle$  are two normalized state vectors, then

$$\langle\psi|\phi\rangle \leq 1. \quad (2.3)$$

In `Quanta $\rho\epsilon\iota$`  the state vector is represented by the `StateVector` class, and the Hamiltonian is correspondingly represented by the `Hamiltonian` class (see `Quanta $\rho\epsilon\iota$`  documentation).

The time evolution of a closed quantum mechanical system is governed by the Schrödinger equation which reads

$$\frac{\partial}{\partial t}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\psi(t)\rangle. \quad (2.4)$$

Quantapεl has a class `StateVectorEvolution` which represents  $|\psi(t)\rangle$  on a given interval of time with a given initial state  $|\psi_0\rangle$ .

A very important quantity for formal manipulations in quantum mechanics is the so-called evolution operator

$$U(t, t_0) = \exp \left\{ -\frac{i}{\hbar} \hat{H}(t - t_0) \right\}. \quad (2.5)$$

If at time  $t = t_0$  we have  $|\psi(t_0)\rangle = |\psi_0\rangle$  then

$$|\psi(t)\rangle = U(t, t_0)|\psi_0\rangle. \quad (2.6)$$

## 2.1 Molecular Hamiltonian

We assume that molecules can be to a certain extent treated within the Born-Oppenheimer approximation. This means that there are some distinguishable electronic states in which we can find the molecule, and that are to some extent independent of the motional states of the nuclei which form the backbone of the molecule. We will assume that a given molecule has an electronic ground state  $|g\rangle$  and an excited state  $|e\rangle$  with certain energies  $\epsilon_g$  and  $\epsilon_e$ , respectively. States  $|g\rangle$  and  $|e\rangle$  are eigenstates of the molecule electronic Hamiltonian and correspondingly, one can write

$$\hat{H}_{\text{mol}} = \epsilon_g |g\rangle\langle g| + \epsilon_e |e\rangle\langle e|. \quad (2.7)$$

This is the simplest bare molecule of interest in Quantapεl.

### 2.1.1 Molecule with a Single Vibrational Mode

To add a single additional degree of freedom (DOF) to the system we have to extend the working Hilbert space. The Hamiltonian, eq. (2.7) describes a single DOF and the corresponding Hilbert space is a vector space defined by all possible linear combinations of vectors  $|g\rangle$  and  $|e\rangle$ . Let us imagine that we deal with a diatomic molecule which oscillates with a characteristic frequency  $\omega$ . Let us assume that the oscillations proceed irrespective of the electronic state in which the molecule finds itself, or in other words, let us assume that the oscillatory DOF of the molecule does not interact with the electronic DOF of the molecule. One can write the Hamiltonian as a sum of the vibrational and electronic parts

$$\hat{H}_{\text{mol}} = \hat{H}_{\text{vib}} + \hat{H}_{\text{el}} = \sum_{n=0}^{\infty} n\hbar\omega |n\rangle\langle n| + \sum_{k=g,e} \epsilon_k |k\rangle\langle k|. \quad (2.8)$$

We disregard the zero point energy of the oscillator as this is only an insignificant shift of the total energy.

The system is now described two sets of states. One is the set of electronic states  $|k\rangle$ ,  $k = g, e$  and one is the set of vibrational states  $|n\rangle$ ,  $n = 1, 2, \dots$ . To

precisely describe the set we have to specify states of both of the components. Possible states of the system are therefore e.g.  $|g\rangle|1\rangle$  or  $|e\rangle|20\rangle$  or any of the linear combinations of such states. Correspondingly, the basis of the common Hilbertspace describing both components of the system has to be composed of the product states  $|k\rangle|n\rangle$ . The components of the Hamiltonian, Eq. (2.8) are not defined on a Hilbert space defined by the product states, but can be easily made so by just assuming that the empty space next to them holds a unity operator on the Hilbert space which we are missing. One can for instance write

$$\sum_{n=0}^{\infty} n\hbar\omega|n\rangle\langle n| = \sum_{n=0}^{\infty} n\hbar\omega|n\rangle\langle n| \otimes \hat{1}_{\text{el}} = \sum_{n=0}^{\infty} n\hbar\omega|n\rangle\langle n| \sum_{k=e,g} |k\rangle\langle k|, \quad (2.9)$$

where  $\hat{1}_{\text{el}}$  is the unity operator on the electronic Hilbert space expressed in the later part of the Eq. (2.9) using the completeness relation

$$\hat{1}_{\text{el}} = \sum_{k=g,e} |k\rangle\langle k|. \quad (2.10)$$

Similarly, we have

$$\sum_{k=g,e} \epsilon_k |k\rangle\langle k| = \sum_{k=g,e} \epsilon_k |k\rangle\langle k| \otimes \hat{1}_{\text{vib}} = \sum_{k=g,e} \epsilon_k |k\rangle\langle k| \sum_n |n\rangle\langle n|. \quad (2.11)$$

The definitions we introduced here allow us for instance to rearrange the Hamiltonian into a form

$$\hat{H}_{\text{mol}} = \left( \epsilon_g + \sum_n n\hbar\omega|n\rangle\langle n| \right) |g\rangle\langle g| + \left( \epsilon_e + \sum_n n\hbar\omega|n\rangle\langle n| \right) |e\rangle\langle e|. \quad (2.12)$$

If we do not insist on writing out the vibrational Hamiltonian using the vibrational eigenstates, we can as well write

$$\sum_n n\hbar\omega|n\rangle\langle n| = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{q}^2. \quad (2.13)$$

This form of the vibrational Hamiltonian will enable us to introduce interaction between the two DOF in a very sensible manner.

## 2.2 Systems of More than One Molecule

## Chapter 3

# Bath Correlation Functions and Spectral Densities

### 3.1 Bath Correlation Function

Bath correlation function is defined as a two point correlation function of the bath part  $\Delta V$  of the system-bath interaction operator, i.e. as

$$C(t) = \frac{1}{\hbar^2} \text{Tr}_B \{ U_B^\dagger(t) \Delta V U_B(t) \Delta V w_{\text{eq}} \} \quad (3.1)$$

where  $w_{\text{eq}}$  is the equilibrium bath density operator,  $U_B(t)$  is the bath evolution operator and the trace is taken over the bath degrees of freedom. The bath correlation function is a complex quantity and as such it has a real part

$$C'(t) = \frac{1}{2} [C(t) + C^*(t)] \quad (3.2)$$

and an imaginary part

$$C''(t) = -\frac{i}{2} [C(t) - C^*(t)] \quad (3.3)$$

so that

$$C(t) = C'(t) + iC''(t) \quad (3.4)$$

### 3.2 Spectral Density

A very important quantity is the Fourier transform of the bath correlation function

$$\tilde{C}(\omega) = \int_0^\infty dt C(t) e^{i\omega t} = 2\text{Re} \int_0^\infty dt C(t) e^{i\omega t} \quad (3.5)$$



It is sometimes referred to as *spectral density*, but we will reserve this name for a different quantity. We will follow Ref. [Mukamel1995]. The Fourier transform  $\tilde{C}(\omega)$  can be split into even and odd parts defined as

$$\tilde{C}'(\omega) = \int_{-\infty}^{\infty} dt C'(t) e^{i\omega t}, \quad \tilde{C}''(\omega) = i \int_{-\infty}^{\infty} dt C''(t) e^{i\omega t} \quad (3.6)$$

so that

$$\tilde{C}(\omega) = \tilde{C}'(\omega) + \tilde{C}''(\omega) \quad (3.7)$$

It can be shown (see [Mukamel1995]) that

$$\tilde{C}(-\omega) = e^{-\frac{\hbar\omega}{k_B T}} \tilde{C}(\omega) \quad (3.8)$$

and

$$\tilde{C}(\omega) = [1 + \coth(\hbar\omega/2k_B T)] \tilde{C}''(\omega) \quad (3.9)$$

Due to the relation between positive and negative frequency values of the Fourier transform of the bath correlation function, we can define it completely through the odd function  $\tilde{C}''(\omega)$  which is a Fourier transform of the imaginary part of the correlation function.

Spectral density

$$J(\omega) = \sum_{\xi} |g_{\xi}|^2 \delta(\omega - \omega_{\xi}) \quad (3.10)$$

## Chapter 4

# Standard Redfield Theory

In this section we define the standard Redfield relaxation tensor in a form which is implemented in Quanta $\rho\epsilon\iota$ . Our formulation is based on the reference [MayKuehn]

### 4.1 General Formula

$$K_n^{(I)}(-\tau) = U_S(\tau) K_n U_S^\dagger(\tau) \quad (4.1)$$

$$\Lambda_m = \sum_n \int_0^\infty d\tau C_{mn}(\tau) K_n^{(I)}(-\tau) \quad (4.2)$$

$$\frac{\partial}{\partial t} \rho(t) = -\frac{i}{\hbar} [H_S, \rho(t)]_- - \mathcal{R}\rho(t) \quad (4.3)$$

$$\begin{aligned} \mathcal{R}\rho(t) = & -\frac{1}{\hbar^2} \sum_m (K_m \Lambda_m \rho(t) + \rho(t) \Lambda_m^\dagger K_m) \\ & + \frac{1}{\hbar^2} \sum_m (K_m \rho(t) \Lambda_m^\dagger + \Lambda_m \rho(t) K_m) \end{aligned} \quad (4.4)$$

#### 4.1.1 Relaxation rate

In a representation of Hamiltonian eigenstates  $|a\rangle$  we can write e.g.

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{aa}(t) = & \sum_b \left( \frac{1}{\hbar^2} \sum_m \langle a | K_m | b \rangle \rho_{bb}(t) \langle b | \Lambda_m^\dagger | a \rangle \right) \\ & + \sum_b \left( \frac{1}{\hbar^2} \sum_m \langle a | \Lambda_m | b \rangle \rho_{bb}(t) \langle b | K_m | a \rangle \right), \end{aligned} \quad (4.5)$$

where we ignored the so-called non-secular terms which connect oscillating coherence elements  $\rho_{ab}$  of the density matrix with the populations  $\rho_{aa}$ . From the definition of  $\Lambda_m$  we have

$$\langle a|\Lambda_m|b\rangle = \sum_n \int_0^\infty d\tau C_{mn}(\tau) e^{-i\omega_{ab}\tau} \langle a|K_n|b\rangle = \sum_n \bar{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle, \quad (4.6)$$

where we used that  $U_S(t) = \sum_a e^{-i\omega_a t} |a\rangle\langle a|$  with  $\omega_a = \epsilon_a/\hbar$  and  $\epsilon_a$  the eigenenergy of the system corresponding to state  $|a\rangle$ . For the element  $\langle a|\Lambda_m^\dagger|b\rangle$  we have  $\langle a|\Lambda_m^\dagger|b\rangle = \langle b|\Lambda_m|a\rangle$  and correspondingly the rate of transfer from  $|b\rangle$  to  $|a\rangle$  is

$$\begin{aligned} \hbar^2 K_{ab} &= \sum_{mn} \bar{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle \langle b|K_m|a\rangle + \bar{C}_{mn}^*(\omega_{ba}) \langle a|K_m|b\rangle \langle a|K_n|b\rangle \\ \hbar^2 K_{ab} &= \sum_{mn} 2\text{Re}\bar{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle \langle b|K_m|a\rangle. \end{aligned} \quad (4.7)$$

We can see that the integral above is a half of the Fourier transform and that there is a relation between the  $\bar{C}(\omega) = \int_0^\infty d\tau C(\tau) e^{i\omega\tau}$  and the full Fourier transform  $\tilde{C}(\omega) = \int_{-\infty}^\infty d\tau C(\tau) e^{i\omega\tau}$  because the correlation function is symmetric

$$C(-t) = C^*(t). \quad (4.8)$$

We can show that

$$2\text{Re}\bar{C}(\omega) = \tilde{C}(\omega), \quad (4.9)$$

and correspondingly

$$\hbar^2 K_{ab} = \sum_{mn} \tilde{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle \langle b|K_m|a\rangle. \quad (4.10)$$

## 4.2 Analytical Results

### 4.2.1 Homo-dimer

The system-bath interaction operators are

$$K_m = |m\rangle\langle m| \quad (4.11)$$

If both energy gap fluctuate with the same energy gap correlation function  $C(t)$ , and the fluctuations on individual sites are independent from each other ( $C_{mn}(t) = \delta_{mn}C(t)$ ), the rate  $K_{ab}$  of the energy transfer from state  $|b\rangle$  to state  $|a\rangle$  reads as (we set  $\hbar = 1$ )

$$K_{ab} = \sum_n |\langle a|n\rangle|^2 |\langle b|n\rangle|^2 \tilde{C}(\omega_{ba}). \quad (4.12)$$

For a homodimer all coefficients  $|\langle b|n\rangle|^2 = \frac{1}{2}$  and the sum over  $n$  gives two contributions which are exactly the same. This means

$$\sum_n |\langle a|n\rangle|^2 |\langle b|n\rangle|^2 = \sum_{n=1}^2 \frac{1}{4} = \frac{1}{2}. \quad (4.13)$$

For an overdamped Brownian oscillator spectral density

$$\tilde{C}''(\omega) = \frac{2\lambda\omega \left(\frac{1}{\tau_c}\right)}{\omega^2 + \left(\frac{1}{\tau_c}\right)^2} \quad (4.14)$$

we have

$$K_{ab} = \frac{1}{2}\tilde{C}'(\omega_{ba}) = \frac{1}{2} \left(1 + \coth\left(\frac{\omega_{ba}}{2k_B T}\right)\right) \frac{2\lambda\omega_{ba} \left(\frac{1}{\tau_c}\right)}{\omega_{ba}^2 + \left(\frac{1}{\tau_c}\right)^2}. \quad (4.15)$$

Given that for a homodimer  $\omega_{12} = 2J$  we have

$$K_{12} = \frac{1}{2}\tilde{C}'(\omega_{21}) = \frac{\lambda J}{2} \frac{1 + \coth\left(\frac{J}{k_B T}\right)}{J^2\tau_c + \frac{\hbar^2}{4\tau_c}}. \quad (4.16)$$

This formula is used to test the calculations of Redfield rates and of the Redfield tensor in *QuantaRel*.

### 4.2.2 Hetero-dimer

## Appendix A

# Microscopic Derivation of Spectral Density Symmetries

Here we will derive the Eqs. (3.8) and (3.9).

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