

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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I. BATH CORRELATION FUNCTIONS AND SPECTRAL DENSITIES

A. Bath Correlation Function

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

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

where w_{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

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

and an imaginary part

$$C''(t) = -\frac{i}{2} [C(t) - C^*(t)] \quad (3)$$

so that

$$C(t) = C'(t) + iC''(t) \quad (4)$$

B. Spectral Density

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

$$\tilde{C}(\omega) = \int_0^\infty dt C(t) e^{i\omega t} = 2\text{Re} \int_0^\infty dt C(t) e^{i\omega t} \quad (5)$$

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

$$\tilde{C}'(\omega) = \int_{-\infty}^\infty dt C'(t) e^{i\omega t}, \quad \tilde{C}''(\omega) = i \int_{-\infty}^\infty dt C''(t) e^{i\omega t} \quad (6)$$

so that

$$\tilde{C}(\omega) = \tilde{C}'(\omega) + \tilde{C}''(\omega) \quad (7)$$

It can be shown (see [Mukamel1995]) that

$$\tilde{C}(-\omega) = e^{-\frac{\hbar\omega}{k_B T}} \tilde{C}(\omega) \quad (8)$$

and

$$\tilde{C}(\omega) = [1 + \coth(\hbar\omega/2k_B T)] \tilde{C}''(\omega) \quad (9)$$

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

$$J(\omega) = \sum_{\xi} |g_{\xi}|^2 \delta(\omega - \omega_{\xi}) \quad (10)$$

II. STANDARD REDFIELD THEORY

In this section we define the standard Redfield relaxation tensor in a form which is implemented in `QuantaRel`. Our formulation is based on the reference [MayKuehn]

A. General Formula

$$K_n^{(I)}(-\tau) = U_S(\tau) K_n U_S^\dagger(\tau) \quad (11)$$

$$\Lambda_m = \sum_n \int_0^\infty d\tau C_{mn}(\tau) K_n^{(I)}(-\tau) \quad (12)$$

$$\frac{\partial}{\partial t} \rho(t) = -\frac{i}{\hbar} [H_S, \rho(t)]_- - \mathcal{R}\rho(t) \quad (13)$$

$$\begin{aligned} \mathcal{R}\rho(t) = & -\frac{1}{\hbar^2} \sum_m (K_m \Lambda_m \rho(t) + \rho(t) \Lambda_m^\dagger K_m) \\ & + \frac{1}{\hbar^2} \sum_m (K_m \rho(t) \Lambda_m^\dagger + \Lambda_m \rho(t) K_m) \end{aligned} \quad (14)$$

1. Relaxation rate

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

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{aa}(t) = & \sum_b \left(\frac{1}{\hbar^2} \sum_m \langle a | K_m | b \rangle \rho_{bb}(t) \langle b | \Lambda_m^\dagger | a \rangle \right) \\ & + \sum_b \left(\frac{1}{\hbar^2} \sum_m \langle a | \Lambda_m | b \rangle \rho_{bb}(t) \langle b | K_m | a \rangle \right), \end{aligned} \quad (15)$$

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

$$\langle a|\Lambda_m|b\rangle = \sum_n \int_0^\infty d\tau C_{mn}(\tau) e^{-i\omega_{ab}\tau} \langle a|K_n|b\rangle = \sum_n \bar{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle, \quad (16)$$

where we used that $U_S(t) = \sum_a e^{-\omega_a t} |a\rangle\langle a|$ with $\omega_a = \epsilon_a/\hbar$ and ϵ_a the eigenergy 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

$$\begin{aligned} \hbar^2 K_{ab} &= \sum_{mn} \bar{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle \langle b|K_m|a\rangle + \bar{C}_{mn}^*(\omega_{ba}) \langle a|K_m|b\rangle \langle a|K_n|b\rangle \\ \hbar^2 K_{ab} &= \sum_{mn} 2\text{Re}\bar{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle \langle b|K_m|a\rangle. \end{aligned} \quad (17)$$

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

$$C(-t) = C^*(t). \quad (18)$$

We can show that

$$2\text{Re}\bar{C}(\omega) = \tilde{C}(\omega), \quad (19)$$

and correspondingly

$$\hbar^2 K_{ab} = \sum_{mn} \tilde{C}_{mn}(\omega_{ba}) \langle a|K_n|b\rangle \langle b|K_m|a\rangle. \quad (20)$$

B. Analytical Results

1. Homo-dimer

The system-bath interaction operators are

$$K_m = |m\rangle\langle m| \quad (21)$$

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 $\hbar = 1$)

$$K_{ab} = \sum_n |\langle a|n\rangle|^2 |\langle b|n\rangle|^2 \tilde{C}(\omega_{ba}). \quad (22)$$

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

$$\sum_n |\langle a|n\rangle|^2 |\langle b|n\rangle|^2 = \sum_{n=1}^2 \frac{1}{4} = \frac{1}{2}. \quad (23)$$

For an overdamped Brownian oscillator spectral density

$$\tilde{C}''(\omega) = \frac{2\lambda\omega \left(\frac{1}{\tau_c}\right)}{\omega^2 + \left(\frac{1}{\tau_c}\right)^2} \quad (24)$$

we have

$$K_{ab} = \frac{1}{2} \tilde{C}(\omega_{ba}) = \frac{1}{2} \left(1 + \coth \left(\frac{\omega_{ba}}{2k_B T} \right) \right) \frac{2\lambda\omega_{ba} \left(\frac{1}{\tau_c} \right)}{\omega_{ba}^2 + \left(\frac{1}{\tau_c} \right)^2}. \quad (25)$$

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

$$K_{12} = \frac{1}{2} \tilde{C}(\omega_{21}) = \frac{\lambda J}{2} \frac{1 + \coth \left(\frac{J}{k_B T} \right)}{J^2 \tau_c + \frac{\hbar^2}{4\tau_c}}. \quad (26)$$

This formula is used to test the calculations of Redfield rates and of the Redfield tensor in Quanta $\rho\epsilon\iota$.

2. Hetero-dimer

Appendix A: Microscopic Derivation of Spectral Density Symmetries

Here we will derive the Eqs. (8) and (9).