Open Quantum Systems Theory behind Quantarhei Package

Tomáš Mančal
Faculty of Mathematics and Physics, Charles University,
Ke Karlovu 5, 121 16 Prague 2, Czech Republic
(Dated: October 3, 2016)

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 gat 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.

CONTENTS

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

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

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

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

and an imaginary part

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

so that

$$C(t) = C'(t) + iC''(t) \tag{4}$$

B. Spectral Density

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

$$\tilde{C}(\omega) = \int\limits_0^\infty \mathrm{d}t\; C(t)e^{i\omega t} = 2\mathrm{Re}\int\limits_0^\infty \mathrm{d}t\; C(t)e^{i\omega t} \tag{5}$$

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

$$\tilde{C}'(\omega) = \int\limits_{-\infty}^\infty \mathrm{d}t\; C'(t)e^{i\omega t},\; \tilde{C}''(\omega) = i\int\limits_{-\infty}^\infty \mathrm{d}t\; C''(t)e^{i\omega t} \tag{6}$$

so that

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

It can be shown (see [Mukamel1995]) that

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

and

$$\tilde{C}(\omega) = [1 + \coth(\hbar\omega/2k_BT)]\, \tilde{C}''(\omega) \tag{9}$$

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

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

Appendix A: Microscopic Derivation of Spectral Density Symmetries

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