

Dissipative evolution of quantum statistical ensembles and nonlinear response to a time-periodic perturbation

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Received 6 June 2003 / Received in final form 26 November 2003

Published online 30 January 2004 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2004

Abstract. We present a detailed discussion of the evolution of a statistical ensemble of quantum mechanical systems coupled weakly to a bath. The Hilbert space of the full system is given by the tensor product between the Hilbert spaces associated with the bath and the bathed system. The statistical states of the ensemble are described in terms of density matrices. Supposing the bath to be held at some – not necessarily thermal – statistical equilibrium and tracing over the bath degrees of freedom, we obtain reduced density matrices defining the statistical states of the bathed system. The master equations describing the evolution of these reduced density matrices are derived under the most general conditions. On time scales that are large with respect to the bath correlation time τ_B^{corr} and with respect to the reciprocal transition frequencies of the bathed system, the resulting evolution of the reduced density matrix of the bathed system is of Markovian type. The detailed balance relations valid for a thermal equilibrium of the bath are derived and the conditions for the validity of the fluctuation-dissipation theorem are given. Based on the general approach, we investigate the non-linear response of the bathed subsystem to a time-periodic perturbation. Summing the perturbation series we obtain the coherences and the populations for arbitrary strengths of the perturbation.

PACS. 05.30.-d Quantum statistical mechanics – 33.35.+r Electron resonance and relaxation – 33.25.+k Nuclear resonance and relaxation

1 Introduction

The evolution of open quantum systems weakly coupled to a bath is a fundamental problem of statistical physics that has been addressed by many authors since the early beginnings of quantum mechanics. The concept of density matrices introduced by von Neumann and Dirac [1,2] in the early thirties of the last century has been extremely useful for the theoretical formulation of the problem. The path-integral method [3–5] offers a practical scheme for the calculation of density matrices describing such subsystems [6,7]. Considering the particular problem of nuclear-spin relaxation in a solid, Bloch, Wangsness, and Redfield have developed a phenomenological approach, in which they derive the Markovian master equation describing the coarse-grained evolution of the reduced density matrix associated with the nuclear spin subsystem [8–10]. Similar formulations have been worked out later on to describe dissipation phenomena in quantum optics [11,12]. Linear-response theory has been invoked by Deutsch et al. [13] to describe the time evolution of macroscopic quantities. Allowing to deal with a large variety of physical situations,

the Bloch-Wangsness-Redfield approach is of great interest. In particular, it provides access to many kinds of rate processes [14], and it can also be applied to the interaction of photons with atoms, clusters or solids [15–17]. The extension of the Bloch-Wangsness-Redfield theory to short times has received a lot of attention in the more recent literature [18–21].

The coarse-grained density matrix of the bathed subsystem, which is the central quantity in the above-mentioned approaches, satisfies the von Neumann conditions of hermiticity and trace preservation, but not that of positivity. Even though, strictly speaking, it is not a true density matrix, it allows a correct description of the coarse-grained evolution of the observables characterizing the considered subsystem. Recently, it was shown [22–31] that it is possible to describe the evolution of the reduced density matrix in such a way that the latter obeys the von Neumann conditions at all times. In the limit of weak interaction and on correspondingly long time scales, the evolution of the density matrix describing the quantum mechanical subsystem becomes strictly Markovian, leading to a quantum dynamical semigroup [23,25–31]. This formulation was generalized later on. In fact, a Markovian

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evolution of an open quantum system weakly interacting with a bath subsystem is expected on time-scales for which memory effects can be neglected [30,31]. The most general form of a generator corresponding to a Markovian evolution of the density matrix of the subsystem has been given by Lindblad [24]. The results presented in references [22–31] are very important, since they ensure that a Markovian evolution of a finite subsystem is compatible with a quantum statistical description of the full system. They also offer a more profound justification of the physical hypotheses underlying the Bloch-Wangsness-Redfield approach. For practical applications, however, both approaches can be considered to be equivalent.

In the present paper, we revisit the Bloch-Wangsness-Redfield formalism. Our principal goal is to obtain a general and transparent quantum-mechanical description of the evolution of two weakly interacting subsystems, where one of the subsystems acts as a bath. The physical properties of both subsystems are described by closed subspaces of their respective Hilbert spaces. Considering subsystems associated with different particles, we exclude mutual quantum-statistical correlations [32]. In accordance with the standard experimental situation, the subsystem acting as a bath is maintained close to some equilibrium by its interaction with the further statistical environment. In order to be as general as possible, we will not specify the nature of the equilibrium of the bath from the very beginning. Thus, our present derivation of the master equations does not rely on the hypothesis of a bath at “thermal” equilibrium. This generalization is e.g. needed to access physical situations, where the equilibrium state of the bath subsystem is controlled by pumping with an intense external laser source. Obviously, the maintenance of the bath at equilibrium is only possible if the bath system interacts with a further statistical environment. The residual interaction is accounted for by introducing a *finite* correlation time τ_B^{corr} of the bath subsystem. This phenomenological parameter allows us to get rid of the further environment and to limit the quantum-mechanical description of the evolution to rather small systems. It is of course understood that the sizes of the considered subsystems must be carefully chosen to catch the relevant dynamics.

Our paper is subdivided into three principal parts. In Section 2 we derive the master equations, which govern the evolution of a subsystem A that interacts weakly with a bath subsystem B . We first introduce the corresponding Hilbert spaces and Hamiltonians as well as the density matrices in the Schrödinger picture (Sect. 2.1). Tracing the subspace associated with the subsystem B , we obtain an effective reduced density matrix that describes the statistical state of the bathed subsystem A . In Section 2.2 we then switch to the interaction picture, which allows us to treat the interaction between both subsystems in an efficient manner. The resulting evolution of the reduced density matrix associated with the subsystem A is presented in Section 2.3, where we also introduce the correlation functions characterizing the bath subsystem B . The last subsections of Section 2 deal with the master equations, which govern the “coarse-grained” evo-

lution of the reduced density matrix. The coarse graining procedure and the underlying hypotheses are presented in Section 2.4. In Section 2.5 we analyze the resulting master equations and we derive the Fermi’s Golden Rule relations. The evolution of the populations and of the coherences in the bathed subsystem A is investigated in Section 2.6, where we consider also the particular situation of a bath at thermal equilibrium.

The following Section 3 focuses on the relaxation of the bathed subsystem. We first discuss the evolution of the expectation values of observables of the bathed subsystem A . As a particular example we then consider the dissipation of energy. We further derive the validity conditions for the fluctuation-dissipation theorem as well as the corresponding relations for a bath with a positive temperature. Starting from the Fourier transforms of the correlation functions, we then verify the Kramers-Kronig relations, which relate the real and the imaginary parts of the susceptibility functions describing either the retarded or the advanced response of the bath subsystem to the perturbation caused by the bathed subsystem (Sect. 4).

Most experimental studies deal with the response of a bathed system to some external perturbation. This situation is addressed in Section 5, where we treat the response to a time-periodic external perturbation to any order in the perturbation. Our final conclusions are drawn in Section 6.

2 Quantum mechanical description of a composite system

2.1 Hilbert spaces and density matrices

We consider an isolated system consisting of two subsystems A and B described by the corresponding Hilbert spaces \mathcal{H}_A and \mathcal{H}_B . The Hilbert space \mathcal{H} of the complete system is given by the tensor product $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$. The dynamics of the system is driven by the time-independent Hamiltonian

$$H = H_0 + H_{\text{int}}, \quad (1)$$

where the first term H_0 describes the free evolution of the subsystems A and B , and where H_{int} represents the interaction between both subsystems. We thus may write

$$H_0 = H_A \otimes \mathbf{1}_B + \mathbf{1}_A \otimes H_B,$$

where the two terms on the right-hand side determine the free evolution of the respective subsystems. The operators $\mathbf{1}_A$ and $\mathbf{1}_B$ denote the identity operators in the Hilbert spaces \mathcal{H}_A and \mathcal{H}_B .

The statistical state of the full system at time t is described by the density matrix $\rho(t)$. Let us recall that $\rho(t)$ is a positive self-adjoint operator with unit trace, i.e., we have

$$\rho(t) = \rho(t)^\dagger, \quad \text{Tr}(\rho(t)) = 1, \quad \rho(t)^2 \leq \rho(t). \quad (2)$$

An observable of the subsystem A is associated with a self-adjoint operator of the form $O_A \otimes \mathbf{1}_B$. Choosing orthonormal basis sets $|a\rangle, a \in \mathcal{A}$ in \mathcal{H}_A and $|b\rangle, b \in \mathcal{B}$ in \mathcal{H}_B , we can write its expectation value

$$\langle O_A \otimes \mathbf{1}_B \rangle = \text{Tr}(\rho(O_A \otimes \mathbf{1}_B))$$

as

$$\langle O_A \otimes \mathbf{1}_B \rangle = \sum_{a, a' \in \mathcal{A}} (\rho_A)_{aa'} \langle a | O_A | a' \rangle,$$

where the matrix

$$(\rho_A)_{aa'} = \sum_{b \in \mathcal{B}} \langle b | \otimes \langle a | \rho | a' \rangle \otimes | b \rangle, \quad (3)$$

satisfying the relations (2), is the reduced density matrix describing the statistical state of the subsystem A . In the following, the partial-trace operation in equation (3) will be abbreviated as

$$\rho_A = \text{Tr}_B(\rho). \quad (4)$$

Similarly, the statistical state of the subsystem B will be written $\rho_B = \text{Tr}_A(\rho)$. The density matrix of the full system $A + B$ can be decomposed as

$$\rho(t) = \rho_A(t) \otimes \rho_B(t) + \eta_{AB}(t),$$

where the first term $\rho_A(t) \otimes \rho_B(t)$ has the properties (2) of a density matrix. The residual self-adjoint operator $\eta_{AB}(t)$ describes the statistical correlation between the subsystems. It satisfies the relations

$$\text{Tr}_B(\eta_{AB}(t)) = 0, \quad \text{Tr}_A(\eta_{AB}(t)) = 0.$$

For vanishing correlation $\eta_{AB}(t) = 0$, the expectation value of an operator of the form $O_A \otimes O_B$ becomes

$$\text{Tr}(\rho(O_A \otimes O_B)) = \langle O_A \rangle \langle O_B \rangle.$$

2.2 Interaction picture

To describe the evolution of the subsystem A interacting with a subsystem B , it is convenient to adopt the interaction picture. The evolution of the full system in the Schrödinger picture is determined by the density matrix

$$\rho(t) = e^{-\frac{i}{\hbar}Ht} \rho(0) e^{\frac{i}{\hbar}Ht},$$

where $\rho(0)$ represents the density matrix at time $t = 0$. The corresponding density matrix in the interaction picture reads

$$\rho^I(t) = e^{\frac{i}{\hbar}H_0t} \rho(t) e^{-\frac{i}{\hbar}H_0t}.$$

Its evolution is governed by

$$\frac{d\rho^I}{dt} = \frac{i}{\hbar} [\rho^I(t), H_{\text{int}}^I(t)] \quad (5)$$

with

$$H_{\text{int}}^I(t) = e^{\frac{i}{\hbar}H_0t} H_{\text{int}} e^{-\frac{i}{\hbar}H_0t}.$$

The partial trace operation Tr_B commutes with the operation corresponding to the change of picture. Thus, using equation (4), we obtain

$$\begin{aligned} \text{Tr}_B(\rho^I(t)) &= e^{\frac{i}{\hbar}H_A t} \text{Tr}_B(\rho(t)) e^{-\frac{i}{\hbar}H_A t} \\ &= (\rho_A(t))^I. \end{aligned}$$

Defining $\rho_A^I(t) \equiv (\rho_A(t))^I$, we get

$$\rho_A^I(t) = \text{Tr}_B(\rho^I(t)),$$

which is the analog of equation (4) in the interaction picture. An observable characterized in the Schrödinger picture by an operator $O(t)$ has the expectation value

$$\langle O(t) \rangle = \text{Tr}(\rho^I(t) O^I(t))$$

with

$$O^I(t) = e^{\frac{i}{\hbar}H_0t} O(t) e^{-\frac{i}{\hbar}H_0t}.$$

2.3 Evolution of the subsystem A weakly coupled to a bath B

The interaction term in the Hamiltonian (1) can always be written

$$H_{\text{int}} = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha},$$

where A_{α} and B_{α} are adequately chosen self-adjoint operators acting in the Hilbert spaces \mathcal{H}_A and \mathcal{H}_B , respectively. In the interaction picture it reads

$$H_{\text{int}}^I(t) = \sum_{\alpha} A_{\alpha}^I(t) \otimes B_{\alpha}^I(t)$$

with

$$A_{\alpha}^I(t) = e^{\frac{i}{\hbar}H_A t} A_{\alpha} e^{-\frac{i}{\hbar}H_A t}$$

and

$$B_{\alpha}^I(t) = e^{\frac{i}{\hbar}H_B t} B_{\alpha} e^{-\frac{i}{\hbar}H_B t}.$$

In the following we restrict our discussion to the case of weakly coupled subsystems A and B . We further suppose that both subsystems are weakly correlated. For vanishing interaction the statistical equilibrium of the subsystem B is described by a density matrix ρ_B^0 , which commutes with the Hamiltonian H_B . The statistical state of the subsystem B is perturbed by the interaction with the subsystem A . The dynamical response of the subsystem B to this perturbation is characterized by the correlation time τ_B^{corr} . In order to catch the dissipative part of the evolution of the

subsystem A , we have to describe the evolution of the density matrix $\rho_A^I(t)$ over a time interval $\Delta t \gg \tau_B^{\text{corr}}$ keeping at least the terms of second order in the interaction.

Under the above assumptions, the subsystem B takes the role of a bath with a finite memory time τ_B^{corr} . The interaction between the subsystems A and B leads to a loss of memory of the subsystem A over large times, so that the evolution of the statistical state of the full system at time t becomes independent of the statistical states $\rho(t')$, $t' < t_0 \ll t$ in the remote past. The statistical state at time t_0 being irrelevant for the evolution at time t , we may assume without loss of generality that the subsystems A and B were uncorrelated at time t_0 , i.e., we set

$$\eta_{AB}(t_0) = 0. \quad (6)$$

According to our above hypotheses, the statistical state of the subsystem B is described by the density matrix

$$\rho_B(t) = \rho_B^0 + \delta\rho_B(t) \quad \text{with} \quad [\rho_B^0, H_B] = 0.$$

The term $\delta\rho_B(t)$ describes the deviations around the equilibrium statistical state ρ_B^0 . These deviations being caused by the interaction with the subsystem A , we have to establish the relation between $\delta\rho_B(t)$ and the evolution of the statistical state of the subsystem A during a time interval $t_0 \leq t < t_0 + \Delta t$. This is done in Appendix A. The first-order terms are cancelled out after the substitutions

$$\begin{aligned} H_A + \sum_{\alpha} A_{\alpha} b_{\alpha}^0 &\rightarrow H_A \\ B_{\alpha} - b_{\alpha}^0 \mathbf{1}_B &\rightarrow B_{\alpha} \end{aligned} \quad (7)$$

with

$$b_{\alpha}^0 = \text{Tr}(\rho_B^0 B_{\alpha}^I(t)) = \text{Tr}(\rho_B^0 B_{\alpha}).$$

Accordingly, the first-order contributions may be taken into account by including a term representing a time-independent ‘‘external field’’ in the Hamiltonian H_A . For example, in the case of the interaction of nuclei with conduction electrons this term would correspond to the so-called Knight shift. In the following we will assume that the replacements (7) have been performed. Then we get (see Appendix A)

$$\begin{aligned} \rho_A^I(t) &= \rho_A^I(t_0) + \left(\frac{i}{\hbar}\right)^2 \\ &\times \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_{\alpha, \beta} \left([\rho_A^I(t_0) A_{\beta}^I(t''), A_{\alpha}^I(t')] \right. \\ &\times c_{\alpha\beta}(t' - t'')^* - [A_{\beta}^I(t'') \rho_A^I(t_0), A_{\alpha}^I(t')] c_{\alpha\beta}(t' - t'') \Big). \end{aligned} \quad (8)$$

The second-order term is determined by the correlation functions

$$\begin{aligned} c_{\alpha\beta}(t' - t'') &= c_{\beta\alpha}(t'' - t')^* \\ &= \text{Tr}(\rho_B^0 B_{\alpha}^I(t') B_{\beta}^I(t'')), \end{aligned} \quad (9)$$

which depend only on the difference $\tau = t' - t''$. This property follows from the fact that the operators ρ_B^0 and H_B commute. In the following we will assume that the correlation functions $c_{\alpha\beta}(\tau)$ vanish for times $\tau > \tau_B^{\text{corr}}$. This condition stands for the loss of memory in the subsystem B , which is caused by its interaction with the further ‘‘statistical’’ environment. It should be noted that the finite correlation time τ_B^{corr} is a purely empirical parameter, which expresses the statistical character of the environment.

2.4 Coarse-grained evolution of the subsystem A

In the following we will focus our attention on the coarse-grained evolution of the subsystem A . Assuming that the subsystem B acts as a bath, we will thus eliminate the physically irrelevant rapid oscillations of $\rho_A^I(t)$ by taking the time-average over a properly chosen coarse-graining time interval Δt . As before, we suppose weak coupling and weak statistical correlations between the subsystems A and B . The subsystem B fluctuates around a statistical equilibrium described by a density matrix ρ_B^0 , which commutes with the free Hamiltonian H_B . The corresponding correlation functions $c_{\alpha\beta}(t' - t'')$ vanish for time differences exceeding the correlation time τ_B^{corr} . It is obvious that the chosen coarse graining time Δt must be larger than the correlation time τ_B^{corr} .

Considering the limited range of the correlation functions $c_{\alpha\beta}(t' - t'')$, we see from equation (8) that the influence of the bath B on the evolution of the subsystem A is efficient only over time intervals $|t' - t''| \leq \tau_B^{\text{corr}}$. It is thus convenient to take $\tau = t' - t''$ instead of t'' as variable of integration. Then the double integral in equation (8) can be rewritten as

$$\begin{aligned} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \dots &= - \int_{t_0}^t dt' \int_{t' - t_0}^0 d\tau \dots \\ &= \int_{t_0}^t dt' \int_0^{t' - t_0} d\tau \dots \\ &\simeq \int_{t_0}^t dt' \int_0^{\infty} d\tau \dots \end{aligned}$$

For the last approximate equality we have used the fact that the correlation functions $c_{\alpha\beta}(\tau)$ vanish for $\tau \geq t' - t_0 \geq t_0 - t_0 \geq \tau_B^{\text{corr}}$. Equation (8) becomes

$$\begin{aligned} \rho_A^I(t) &= \rho_A^I(t_0) + \left(\frac{i}{\hbar}\right)^2 \\ &\times \int_{t_0}^t dt' \int_0^{\infty} d\tau \sum_{\alpha, \beta} \left([\rho_A^I(t_0) A_{\beta}^I(t' - \tau), A_{\alpha}^I(t')] \right. \\ &\times c_{\alpha\beta}(\tau)^* - [A_{\beta}^I(t' - \tau) \rho_A^I(t_0), A_{\alpha}^I(t')] c_{\alpha\beta}(\tau) \Big). \end{aligned}$$

Note that the above expression is independent of t_0 . In order to render it more transparent, we adopt the orthonormal basis $\{|a\rangle, a \in \mathcal{A}\}$ in \mathcal{H}_A that diagonalizes the free

Hamiltonian H_A . Assuming the Hamiltonian H_A to possess a discrete spectrum, we have

$$H_A |a\rangle = E_a |a\rangle, \quad \forall a \in \mathcal{A}$$

and

$$\langle a | A_\alpha^I(t) | a' \rangle = \langle a | A_\alpha | a' \rangle e^{i\omega_{aa'}t}$$

with $\omega_{aa'} = (E_a - E_{a'})/\hbar$. For the matrix elements of the density matrix $\rho_A^I(t)$ we get

$$\begin{aligned} \langle a_1 | \rho_A^I(t) | a_2 \rangle &= \langle a_1 | \rho_A^I(t_0) | a_2 \rangle \\ &+ \sum_{a'_1, a'_2 \in \mathcal{A}} \Gamma_{a_1 a_2}^{a'_1 a'_2} \langle a'_1 | \rho_A^I(t_0) | a'_2 \rangle \int_{t_0}^t e^{i(\omega_{a_1 a_2} - \omega_{a'_1 a'_2})t'} dt'. \end{aligned} \quad (10)$$

The coefficients $\Gamma_{a_1 a_2}^{a'_1 a'_2}$ are given by

$$\begin{aligned} \Gamma_{a_1 a_2}^{a'_1 a'_2} &= \Gamma_{a_2 a_1}^{a'_2 a'_1} * \\ &= F_{a_1 a_2}^{a'_1 a'_2} - \delta_{a_1}^{a'_1} \sum_{a \in \mathcal{A}} F_{aa}^{a_2 a'_2} \\ &\quad + \left(F_{a_2 a_1}^{a'_2 a'_1} - \delta_{a_2}^{a'_2} \sum_{a \in \mathcal{A}} F_{aa}^{a_1 a'_1} \right) * \end{aligned} \quad (11)$$

with

$$\begin{aligned} F_{a_1 a_2}^{a'_1 a'_2} &= \frac{1}{\hbar^2} \sum_{\alpha\beta} \langle a_1 | A_\alpha | a'_1 \rangle \langle a'_2 | A_\beta | a_2 \rangle \\ &\quad \times \int_{-\infty}^0 c_{\beta\alpha}(\tau) e^{i\omega_{a_2 a_2} \tau} d\tau. \end{aligned} \quad (12)$$

The correlation functions $c_{\alpha\beta}(\tau)$ have been defined in equation (9). After evaluation of the time integral in equation (10) we obtain finally

$$\begin{aligned} \langle a_1 | \rho_A^I(t) | a_2 \rangle &= \langle a_1 | \rho_A^I(t_0) | a_2 \rangle \\ &+ \Delta t \sum_{a'_1, a'_2 \in \mathcal{A}} \Gamma_{a_1 a_2}^{a'_1 a'_2} \langle a'_1 | \rho_A^I(t_0) | a'_2 \rangle \\ &\quad \times g((\omega_{a_1 a_2} - \omega_{a'_1 a'_2})\Delta t) \\ &\quad \times e^{i(\omega_{a_1 a_2} - \omega_{a'_1 a'_2})\bar{t}} \end{aligned} \quad (13)$$

with

$$\Delta t = t - t_0 \quad \bar{t} = t_0 + \frac{\Delta t}{2} \quad (14)$$

and

$$g(x) = \frac{\sin(x/2)}{x/2}.$$

Equation (13) gives us the desired time dependence of the statistical state of the subsystem A interacting with the bath subsystem B . It is the basis for our following

derivation of the so-called master equations, which govern the “coarse grained” evolution of the subsystem A .

The absolute values of the exact matrix elements $\langle a_1 | \rho_A^I(t) | a_2 \rangle$ are bounded by 1. This follows from equation (2), which implies that

$$\begin{aligned} \sum_{a_1, a_2 \in \mathcal{A}} |\langle a_1 | \rho_A^I(t) | a_2 \rangle|^2 &\equiv \text{Tr}(\rho_A^I(t)^2) \\ &\leq \text{Tr}(\rho_A^I(t)) = 1. \end{aligned}$$

This property restricts the validity range of equation (13) to time intervals $\Delta t \gg \tau_B^{\text{corr}}$ that are small enough to satisfy the condition $0 < \rho_A^I(t)^2 \leq \rho_A^I(t)$, which will be referred to as the “positivity condition”. Note that the approximate density matrix $\rho_A^I(t)$ provided by equation (13) is already self-adjoint and that it satisfies also $\text{Tr}(\rho_A^I(t)) = 1$.

Our present purpose is to obtain a system of equations governing the so-called “coarse grained” evolution. In other words, we are looking for the equations, which govern the time evolution of a “time-averaged” density matrix $\rho_A^I(\bar{t})$, where the time averaging suppresses the oscillations generated by the bath. We define the time-averaged density matrix $D_{A,R}^I(\bar{t})$ by

$$D_{A,R}^I(\bar{t}) = \frac{1}{\Delta t} \int_{\bar{t}-\Delta t/2}^{\bar{t}+\Delta t/2} \rho_A^I(t') dt' \quad (15)$$

with

$$\tau_B^{\text{corr}} \ll \Delta t \ll \pi/\omega_{max}, \quad (16)$$

where

$$\omega_{max} = \max\{|\omega_{a_1 a_2}|\}, \quad a_1, a_2 \in \mathcal{A}$$

denotes the maximal transition frequency. Similar to $\rho_A^I(t)$, the operator $D_{A,R}^I(\bar{t})$ (15) is self-adjoint with unit trace. We note, however, that the time-averaged density matrix $D_{A,R}^I(\bar{t})$ does not strictly satisfy the positivity condition.

Equation (16) allows us to use the approximate identity

$$g((\omega_{a_1 a_2} - \omega_{a'_1 a'_2})\Delta t) = 1.$$

Then, according to the relations (13), the evolution of the density matrix $\rho_A^I(t)$ is basically governed by two different types of behavior. On the one hand, terms with $\omega_{a_1 a_2} - \omega_{a'_1 a'_2} \simeq 0$ lead to a change increasing linearly with time. On the other hand, terms corresponding to difference frequencies significantly different from zero give rise to oscillating contributions. Obviously, a clear cut separation between the two types of behavior is only possible if both contributions act on different time scales. Defining the “evolution time” τ_A^{evol} by the reciprocal value of this slope, we first consider equation (13) under the condition

$$\tau_B^{\text{corr}} \ll \Delta t < \pi/\omega_{max} \ll \tau_A^{\text{evol}}. \quad (17)$$

From the definitions (15) and (14) it follows that

$$\frac{d D_{A,R}^I(\bar{t})}{d\bar{t}} = \frac{\rho_A^I(t) - \rho_A^I(t_0)}{t - t_0}.$$

Thus, making use of equation (17), we get from equation (13)

$$\frac{d \langle a_1 | D_{A,R}^I(\bar{t}) | a_2 \rangle}{d\bar{t}} = \sum_{a'_1, a'_2 \in \mathcal{A}} \Gamma_{a'_1 a'_2}^{a'_1 a'_2} \langle a'_1 | \rho_A^I(t_0) | a'_2 \rangle e^{i(\omega_{a_1 a_2} - \omega_{a'_1 a'_2})\bar{t}}.$$

For the considered time intervals satisfying the condition (16), the matrix elements of $\rho_A^I(t_0)$ on the right-hand side can be replaced by the respective matrix elements of the operator $D_{A,R}^I(\bar{t})$. We then get the Redfield equations [8–10]

$$\frac{d \langle a_1 | D_{A,R}^I(\bar{t}) | a_2 \rangle}{d\bar{t}} = \sum_{a'_1, a'_2 \in \mathcal{A}} \Gamma_{a'_1 a'_2}^{a'_1 a'_2} \langle a'_1 | D_{A,R}^I(\bar{t}) | a'_2 \rangle e^{i(\omega_{a_1 a_2} - \omega_{a'_1 a'_2})\bar{t}}. \quad (18)$$

When considering the effects of external forces, it is convenient to change to a Schrödinger-like picture, in order to get rid of the spurious time-dependence introduced by the change to the interaction picture. We then have to consider the evolution of the matrix

$$D_{A,R}(\bar{t}) = e^{-\frac{i}{\hbar} H_A \bar{t}} D_{A,R}^I(\bar{t}) e^{\frac{i}{\hbar} H_A \bar{t}}. \quad (19)$$

From equation (18) we find

$$\begin{aligned} \frac{d}{d\bar{t}} \langle a_1 | D_{A,R}(\bar{t}) | a_2 \rangle &= \\ \frac{i}{\hbar} \langle a_1 | [D_{A,R}(\bar{t}), H_A] | a_2 \rangle &+ \\ + \sum_{a'_1, a'_2 \in \mathcal{A}} \Gamma_{a'_1 a'_2}^{a'_1 a'_2} \langle a'_1 | D_{A,R}(\bar{t}) | a'_2 \rangle. & \quad (20) \end{aligned}$$

The “master equations” (18) and (20) govern the coarse grained evolution of the time-averaged reduced density matrix of the subsystem A interacting with the bath B .

In many situations the oscillatory contributions to the Redfield equations (18) are irrelevant. Obviously, the slowest oscillations are determined by

$$\Delta\omega_A = \inf\{|\omega_{a_1 a_2} - \omega_{a'_1 a'_2}| \neq 0, \quad a_1, a_2, a'_1, a'_2 \in \mathcal{A}\}.$$

This quantity is different from zero, since according to our assumptions the subsystem A possesses only a finite number N of energy levels. Obviously, linear and oscillatory contributions to the evolution of the time-averaged density matrix are well distinguished if

$$2\pi/\Delta\omega_A \ll \tau_A^{\text{evol}}.$$

Performing the time average in equation (15) over time intervals Δt satisfying

$$\tau_B^{\text{corr}} \ll \pi/\omega_{max} < 2\pi/\Delta\omega_A \ll \Delta t \ll \tau_A^{\text{evol}},$$

instead of the condition (17), we find that even the slowest oscillatory terms in equation (18) disappear under the averaging procedure and that only terms with $\omega_{a'_1 a'_2} = \omega_{a_1 a_2}$ contribute. Then the resulting evolution of the time-averaged density matrix $D_A^I(\bar{t})$ becomes Markovian, i.e., we get

$$\begin{aligned} \frac{d \langle a_1 | D_A^I(\bar{t}) | a_2 \rangle}{d\bar{t}} &= \\ = \sum_{\{a'_1, a'_2 | \omega_{a'_1 a'_2} = \omega_{a_1 a_2}\}} \Gamma_{a'_1 a'_2}^{a'_1 a'_2} \langle a'_1 | D_A^I(\bar{t}) | a'_2 \rangle. & \quad (21) \end{aligned}$$

In order to simplify our terminology, we will from now on refer to these equations as the master equations governing the Markovian coarse-grained evolution or the Markovian master equations. Switching to the Schrödinger picture, we get in full analogy with equations (19, 20)

$$D_A(\bar{t}) = e^{-\frac{i}{\hbar} H_A \bar{t}} D_A^I(\bar{t}) e^{\frac{i}{\hbar} H_A \bar{t}}$$

and

$$\begin{aligned} \frac{d}{d\bar{t}} \langle a_1 | D_A(\bar{t}) | a_2 \rangle &= \\ \frac{i}{\hbar} \langle a_1 | [D_A(\bar{t}), H_A] | a_2 \rangle &+ \\ + \sum_{\{a'_1, a'_2 | \omega_{a'_1 a'_2} = \omega_{a_1 a_2}\}} \Gamma_{a'_1 a'_2}^{a'_1 a'_2} \langle a'_1 | D_A(\bar{t}) | a'_2 \rangle. & \quad (22) \end{aligned}$$

In contrast with the Redfield equation (18), the Markovian coarse-grained evolution of the averaged density matrix $D_A^I(\bar{t})$ (21) is already fully determined by the coefficients $\Gamma_{a'_1 a'_2}^{a'_1 a'_2}$ with $\omega_{a'_1 a'_2} = \omega_{a_1 a_2}$. The Redfield equation (18) becomes relevant if one looks for the system response to an external time-periodic field with frequencies of the order of the transition energies. Such a situation is e.g. encountered in NMR experiments under stationary conditions.

A lot of important physical properties can be adequately treated with the Markovian master equations. We will thus limit most of our following discussions to equations (21, 22). The principal simplifications resulting from the restriction to the subset of the Γ coefficients will be discussed in Sections 2.5 and 2.6.

2.5 Markovian coarse-grained evolution:

Structure of the coefficients $\Gamma_{a'_1 a'_2}^{a'_1 a'_2}$

In this subsection we will rearrange the master equations (22) in order to get a better insight into the mechanisms governing the Markovian coarse-grained evolution.

Starting from equation (11), we can rewrite the coefficients $\Gamma_{a_1 a_2}^{a_1' a_2'}$ in equations (21, 18) in the form

$$\Gamma_{a_1 a_2}^{a_1' a_2'} = \Gamma_{0 a_1 a_2}^{a_1' a_2'} - \frac{1}{\hbar} \left(\delta_{a_1}^{a_1'} G_{a_2' a_2} + \delta_{a_2}^{a_2'} G_{a_1 a_1'} \right) + \frac{i}{\hbar} \left(\delta_{a_1}^{a_1'} \Delta H_{a_2' a_2} - \delta_{a_2}^{a_2'} \Delta H_{a_1 a_1'} \right) \quad (23)$$

with

$$\Gamma_{0 a_1 a_2}^{a_1' a_2'} \equiv \left(\Gamma_{0 a_2 a_1}^{a_2' a_1'} \right)^* = F_{a_1 a_2}^{a_1' a_2'} + \left(F_{a_2 a_1}^{a_2' a_1'} \right)^*, \quad (24)$$

$$G_{aa'} = \frac{\hbar}{2} \sum_{a'' \in \mathcal{A}} \Gamma_{0 a'' a}^{a' a''}, \quad (25)$$

and

$$\Delta H_{aa'} = \frac{i \hbar}{2} \sum_{a'' \in \mathcal{A}} \left(F_{a'' a}^{a' a''} - \left(F_{a'' a''}^{a' a''} \right)^* \right). \quad (26)$$

The first two terms in equation (23) give rise to the irreversible evolution of the subsystem A . The operators G and ΔH_A describe the effective dynamical coupling between the states of the bath system A that is induced by the polarization of the bath subsystem B , which – in turn – is a consequence of its interaction with the subsystem A . While the operator G ensures the conservation of the trace of the time-averaged density matrix $D_A(\bar{t})$, the operator ΔH_A leads to a correction of the Hamiltonian H_A . In other words, ΔH_A represents a self-energy operator.

The master equations in the Schrödinger picture, equations (20, 22), may be rewritten as

$$\frac{d}{dt} D_A(\bar{t}) = \frac{i}{\hbar} [D_A(\bar{t}), H_A] + \Gamma(D_A(\bar{t})), \quad (27)$$

where Γ is a linear superoperator acting on $\mathcal{L}(\mathcal{H}_A)$,

$\Gamma(X) =$

$$\Gamma_0(X) + \frac{i}{\hbar} (X (\Delta H_A + iG_A) - (\Delta H_A - iG_A) X), \quad (28)$$

$\forall X \in \mathcal{L}(\mathcal{H}_A)$

with

$$\langle a_1 | \Gamma_0(X) | a_2 \rangle = \sum_{a_1', a_2' \in \mathcal{A}} \Gamma_{0 a_1 a_2}^{a_1' a_2'} \langle a_1' | X | a_2' \rangle. \quad (29)$$

Here and in the following Section 2.6 we will assume that the restriction of the summation in equations (21, 22) is justified. It can be replaced by adopting the convention

$$\Gamma_{a_1 a_2}^{a_1' a_2'} = \Gamma_{0 a_1 a_2}^{a_1' a_2'} = 0 \quad \text{for} \quad \omega_{a_1' a_2'} \neq \omega_{a_1 a_2}. \quad (30)$$

Since then we have only to consider the case $\omega_{a_1' a_2'} = \omega_{a_1 a_2}$, we obtain from the expression (12) for the coefficients $F_{a_1 a_2}^{a_1' a_2'}$

$$F_{a_1 a_2}^{a_1' a_2'} \pm \left(F_{a_2 a_1}^{a_2' a_1'} \right)^* = \frac{1}{\hbar} \sum_{\alpha \beta} \langle a_1 | A_\alpha | a_1' \rangle \langle a_2' | A_\beta | a_2 \rangle \begin{cases} \chi_{\beta\alpha}(\omega_{a_1' a_1}) \\ i\bar{\chi}_{\beta\alpha}(\omega_{a_1' a_1}) \end{cases} \quad (31)$$

with

$$\chi_{\alpha\beta}(\omega) = \frac{1}{\hbar} \int_{-\infty}^{\infty} c_{\alpha\beta}(\tau) e^{i\omega\tau} d\tau \quad (32)$$

and

$$\bar{\chi}_{\alpha\beta}(\omega) = \frac{i}{\hbar} \int_{-\infty}^{\infty} \epsilon(\tau) c_{\alpha\beta}(\tau) e^{i\omega\tau} d\tau, \quad (33)$$

where the function $\epsilon(\tau)$ in the last integral represents the Heaviside function

$$\epsilon(\tau) = \begin{cases} -1 & \text{if } \tau < 0 \\ 0 & \text{if } \tau = 0 \\ 1 & \text{if } \tau > 0. \end{cases}$$

The functions $\chi_{\alpha\beta}(\omega)$ and $\bar{\chi}_{\alpha\beta}(\omega)$ are connected by Kramers-Kronig relations (see Sect. 4). From the symmetry property (9) of the correlation functions $c_{\alpha\beta}(t' - t'')$ it follows that $\forall \alpha, \beta$ and $\omega \in \mathbb{R}$

$$\begin{aligned} \chi_{\alpha\beta}(\omega)^* &= \chi_{\beta\alpha}(\omega), \\ \bar{\chi}_{\alpha\beta}(\omega)^* &= \bar{\chi}_{\beta\alpha}(\omega). \end{aligned}$$

In order to specify the coefficients $\Gamma_{a_1 a_2}^{a_1' a_2'}$ it is convenient to introduce the basis set $|b\rangle, b \in \mathcal{B}$ provided by the eigenvectors of H_B and ρ_B^0 . Since presently the spectra of these operators are assumed to be discrete, we have

$$H_B |b\rangle = E_b |b\rangle, \quad \rho_B^0 |b\rangle = p_b |b\rangle,$$

and the correlation functions (9) become

$$c_{\alpha\beta}(\tau) = \sum_{b, b' \in \mathcal{B}} p_b \langle b | B_\alpha | b' \rangle \langle b' | B_\beta | b \rangle e^{-i\omega_{b'b}\tau}. \quad (34)$$

Insertion into equations (32, 33) yields

$$\begin{aligned} \chi_{\alpha\beta}(\omega) &= \\ & \frac{2\pi}{\hbar} \sum_{b, b' \in \mathcal{B}} p_b \langle b | B_\alpha | b' \rangle \langle b' | B_\beta | b \rangle \delta(\omega - \omega_{b'b}), \end{aligned} \quad (35)$$

$$\begin{aligned} \bar{\chi}_{\alpha\beta}(\omega) &= \\ & - \frac{2}{\hbar} \sum_{b, b' \in \mathcal{B}} p_b \langle b | B_\alpha | b' \rangle \langle b' | B_\beta | b \rangle \frac{1}{\omega - \omega_{b'b}}. \end{aligned} \quad (36)$$

The matrix $\chi_{\alpha\beta}(\omega)$ is positive, since for any

$$X = \sum_{\alpha} x_{\alpha} B_{\alpha}, \quad x_{\alpha} \in \mathbb{C}, \quad \forall \alpha$$

we get immediately

$$\sum_{\alpha, \beta} x_{\alpha}^* \chi_{\alpha\beta}(\omega) x_{\beta} = \frac{2\pi}{\hbar} \sum_{b, b' \in \mathcal{B}} p_b |\langle b' | X | b \rangle|^2 \delta(\omega - \omega_{b'b}) \geq 0. \quad (37)$$

From the definition (24) and equation (31) we then obtain that the coefficients $\Gamma_{0 a_1 a_2}^{a'_1 a'_2}$ can be written as a positive hermitian form, i.e.,

$$\Gamma_{0 a_1 a_2}^{a'_1 a'_2} = \frac{1}{\hbar} \sum_{\alpha\beta} y_\beta^* \chi_{\beta\alpha}(\omega_{a'_1 a_1}) x_\alpha \quad (38)$$

with the vectors

$$x_\alpha = \langle a_1 | A_\alpha | a'_1 \rangle, \quad y_\beta = \langle a_2 | A_\beta | a'_2 \rangle.$$

For $a_1 = a_2$ and $a'_1 = a'_2$ they are real positive, i.e.,

$$\Gamma_{0 a a}^{a' a'} \geq 0. \quad (39)$$

The Cauchy-Schwarz inequality for positive hermitian forms implies

$$|\Gamma_{0 a_1 a_2}^{a'_1 a'_2}| \leq \sqrt{\Gamma_{0 a_1 a_1}^{a'_1 a'_1}} \sqrt{\Gamma_{0 a_2 a_2}^{a'_2 a'_2}}.$$

In particular, we have

$$\text{Re}(\Gamma_{0 a_1 a_2}^{a_1 a_2}) \leq \sqrt{\Gamma_{0 a_1 a_1}^{a_1 a_1}} \sqrt{\Gamma_{0 a_2 a_2}^{a_2 a_2}}.$$

Exploiting equations (23, 24, 25, 26), we get

$$\begin{aligned} \text{Re}(\Gamma_{0 a_1 a_2}^{a_1 a_2}) &\leq \sqrt{\Gamma_{0 a_1 a_1}^{a_1 a_1}} \sqrt{\Gamma_{0 a_2 a_2}^{a_2 a_2}} - \frac{1}{2} \sum_{a' \in \mathcal{A}} (\Gamma_{0 a' a_1}^{a_1 a_1} + \Gamma_{0 a' a_2}^{a_2 a_2}) \\ &= -\frac{1}{2} \left(\left(\sqrt{\Gamma_{0 a_1 a_1}^{a_1 a_1}} - \sqrt{\Gamma_{0 a_2 a_2}^{a_2 a_2}} \right)^2 \right. \\ &\quad \left. + \sum_{\{a' | a' \neq a_1\}} \Gamma_{0 a' a_1}^{a_1 a_1} + \sum_{\{a' | a' \neq a_2\}} \Gamma_{0 a' a_2}^{a_2 a_2} \right) \\ &\leq 0. \end{aligned} \quad (40)$$

The inequality on the last line is found from equation (39). These relations will be useful for our discussion of the coherences in Section 2.6.

Equation (25) defines a self-adjoint operator G_A . The coarse-graining condition equation (30) implies that its matrix elements

$$\langle a | G_A | a' \rangle \equiv G_{aa'}, \quad \forall a, a' \in \mathcal{A}$$

are zero for $\omega_{aa'} \neq 0$. Thus, the spectral subspaces of the free Hamiltonian H_A remaining unchanged under the action of G_A , we have

$$[G_A, H_A] = 0.$$

Adopting a basis that diagonalizes simultaneously both operators G_A and H_A , we find from the definition (25) and equations (37, 38)

$$G_A \geq 0.$$

Similarly, equation (26) defines the matrix elements of the self-adjoint self-energy operator ΔH_A

$$\begin{aligned} \langle a | \Delta H_A | a' \rangle &\equiv \Delta H_{aa'} \\ &= -\frac{1}{2} \sum_{a'' \in \mathcal{A}} \sum_{\alpha\beta} \langle a | A_\alpha | a'' \rangle \langle a'' | A_\beta | a' \rangle \\ &\quad \times \bar{\chi}_{\alpha\beta}(\omega_{aa''}). \end{aligned} \quad (41)$$

Again, these matrix elements are zero for $\omega_{aa'} \neq 0$, so that

$$[\Delta H_A, H_A] = 0.$$

For $\omega_{aa'} = 0$ we get from equations (36, 41)

$$\begin{aligned} \langle a | \Delta H_A | a' \rangle &= \sum_{a'' \in \mathcal{A}} \sum_{b, b'' \in \mathcal{B}} p_b \frac{\langle b, a | H_{\text{int}} | a'', b'' \rangle \langle b'', a'' | H_{\text{int}} | a', b \rangle}{E_a + E_b - E_{a''} - E_{b''}}, \end{aligned}$$

where $\langle b, a | H_{\text{int}} | a'', b'' \rangle$ stands for $\langle b | \otimes \langle a | H_{\text{int}} | a'' \rangle \otimes | b'' \rangle$.

In most cases the matrix elements of the self-energy operator $\langle a | \Delta H_A | a' \rangle$ will be rather small, so that ΔH_A can be neglected. Otherwise the contributions of ΔH_A can normally be removed using conventional renormalization procedures. Then equation (23) simplifies to

$$\begin{aligned} \Gamma_{a_1 a_2}^{a'_1 a'_2} &\simeq \Gamma_R^{a'_1 a'_2} \\ &= \Gamma_{0 a_1 a_2}^{a'_1 a'_2} - \frac{1}{\hbar} \left(\delta_{a_1}^{a'_1} G_{a'_2 a_2} + \delta_{a_2}^{a'_2} G_{a_1 a_1} \right). \end{aligned}$$

Inserting the expression (35) for $\chi_{\alpha\beta}(\omega)$ into equation (38), we get for $\omega_{a'_1 a_1} = \omega_{a'_2 a_2}$

$$\begin{aligned} \Gamma_{0 a_1 a_2}^{a'_1 a'_2} &= \frac{2\pi}{\hbar} \sum_{b, b'' \in \mathcal{B}} p_b \langle b, a'_1 | H_{\text{int}} | a_2, b'' \rangle \langle b'', a_1 | H_{\text{int}} | a'_1, b \rangle \\ &\quad \times \delta(E_{a'_1} + E_b - E_{a_1} - E_{b''}). \end{aligned}$$

In particular,

$$\begin{aligned} \Gamma_{a \rightarrow a'} &\equiv \Gamma_{0 a' a'}^{a a} = \frac{2\pi}{\hbar} \sum_{b, b'' \in \mathcal{B}} p_b |\langle b, a | H_{\text{int}} | a', b'' \rangle|^2 \delta(E_a + E_b - E_{a'} - E_{b''}) \end{aligned} \quad (42)$$

is the transition rate corresponding to Fermi's Golden Rule, where the statistical equilibrium of the subsystem B is taken into account via the probability distributions p_b .

2.6 Coarse-grained evolution of the populations, coherences and detailed balance relations

For simplicity, let us suppose that the energy splittings $\hbar\omega_{aa'}$ are all different and non-zero, so that we have a

one-to-one correspondence between $\omega_{aa'}$ and the energy levels E_a and $E_{a'}$. Then the condition $\omega_{a'_1 a_1} = \omega_{a'_2 a_2}$ implies $a_1 = a_2$ and $a'_1 = a'_2$. According to equation (21), the evolution of the diagonal elements of the coarse-grained density matrix, usually referred to as “populations”, is governed by

$$\frac{d \langle a | D_A^I(\bar{t}) | a \rangle}{d\bar{t}} = \sum_{a' \in \mathcal{A}} \Gamma_{a a'}^{a' a'} \langle a' | D_A^I(\bar{t}) | a' \rangle. \quad (43)$$

Inspection of equation (23) shows that

$$\Gamma_{a a'}^{a' a'} = \Gamma_{0 a a'} \equiv \Gamma_{a' \rightarrow a} \quad \text{for} \quad a \neq a'.$$

For $a = a'$ we get from equations (23, 25)

$$\Gamma_{aa}^{aa} = \Gamma_{0 aa}^{aa} - \sum_{a' \in \mathcal{A}} \Gamma_{0 a' a}^{a a'} = - \sum_{\{a' | a' \neq a\}} \Gamma_{a \rightarrow a'}. \quad (44)$$

Thus, equations (43) becomes

$$\begin{aligned} \frac{d \langle a | D_A^I(\bar{t}) | a \rangle}{d\bar{t}} = & \sum_{\{a' | a' \neq a\}} \Gamma_{a' \rightarrow a} \langle a' | D_A^I(\bar{t}) | a' \rangle - \Gamma_{a \rightarrow a'} \langle a | D_A^I(\bar{t}) | a \rangle. \end{aligned} \quad (45)$$

Supposing now the bath to be in thermal equilibrium, we have

$$p_b = \frac{1}{Z_B} e^{-E_b/k_B T} \quad \text{with} \quad Z_B = \sum_{b \in \mathcal{B}} e^{-E_b/k_B T},$$

where T is the temperature of the bath, and k_B denotes the Boltzmann constant. Equation (42) then becomes

$$\begin{aligned} \Gamma_{a \rightarrow a'} = & \frac{2\pi}{\hbar} \sum_{b, b' \in \mathcal{B}} \frac{1}{Z_B} e^{-E_b/k_B T} |\langle b, a | H_{\text{int}} | a', b' \rangle|^2 \\ & \times \delta(E_a + E_b - E_{a'} - E_{b'}) \\ = & \frac{2\pi}{\hbar} \sum_{b, b' \in \mathcal{B}} \frac{1}{Z_B} e^{(E_a - E_{a'} - E_{b'})/k_B T} |\langle b, a | H_{\text{int}} | a', b' \rangle|^2 \\ & \times \delta(-E_a - E_b + E_{a'} + E_{b'}), \end{aligned}$$

which implies

$$\frac{\Gamma_{a \rightarrow a'}}{\Gamma_{a' \rightarrow a}} = \frac{e^{E_a/k_B T}}{e^{E_{a'}/k_B T}}.$$

Inserting the above relation into equation (45), we get the equilibrium condition

$$\begin{aligned} \sum_{\{a' | a' \neq a\}} \Gamma_{a' \rightarrow a} \left(\langle a' | D_A^I(\bar{t}) | a' \rangle \right. \\ \left. - e^{(E_a - E_{a'})/k_B T} \langle a | D_A^I(\bar{t}) | a \rangle \right) = 0. \end{aligned}$$

This condition holding for arbitrary temperature, we find

$$\langle a | D_A^I(\bar{t}) | a \rangle = \frac{1}{Z_A} e^{-E_a/k_B T} \quad (46)$$

with

$$Z_A = \sum_{a \in \mathcal{A}} e^{-E_a/k_B T},$$

or the equivalent “detailed-balance” relations

$$\Gamma_{a' \rightarrow a} \langle a' | D_A^I(\bar{t}) | a' \rangle - \Gamma_{a \rightarrow a'} \langle a | D_A^I(\bar{t}) | a \rangle = 0, \quad \forall a, a' \in \mathcal{A}.$$

Equation (46) shows that the subsystem A tends toward a thermal equilibrium, the temperature being that of the bath. Note that this result is independent of any high-temperature approximation.

The evolution of the coherences for $a_1 \neq a_2$ is obtained from

$$\frac{d \langle a_1 | D_A^I(\bar{t}) | a_2 \rangle}{d\bar{t}} = \Gamma_{a_1 a_2}^{a_1 a_2} \langle a_1 | D_A^I(\bar{t}) | a_2 \rangle.$$

According to equation (40) the real part of $\Gamma_{a_1 a_2}^{a_1 a_2}$ is negative or zero, i.e., as expected, the coherences cannot increase with time.

3 Irreversible evolution and energy dissipation

The “coarse-grained” expectation value of an observable of the subsystem A , characterized by a self-adjoint operator O_A and independent of time in the Schrödinger picture, is given by

$$\langle O_A \rangle(\bar{t}) = \text{Tr}(D_A(\bar{t}) O_A). \quad (47)$$

From equations (27, 28, 29) we obtain

$$\begin{aligned} \frac{d}{d\bar{t}} \langle O_A \rangle(\bar{t}) = & \left\langle \frac{i}{\hbar} [H_A + \Delta H_A, O_A] \right\rangle(\bar{t}) \\ & - \frac{1}{\hbar} \langle \{G_A, O_A\} \rangle(\bar{t}) \\ & + \text{Tr}(O_A \Gamma_0(D_A(\bar{t}))). \end{aligned} \quad (48)$$

Replacing O_A by H_A in equation (47), we get the mean energy of the subsystem A ,

$$E_A(\bar{t}) = \text{Tr}(D_A(\bar{t}) H_A).$$

From equation (48) and using the definition (25) of $G_{aa'}$, we obtain for its evolution

$$\begin{aligned} \frac{dE_A(\bar{t})}{d\bar{t}} = & \sum_{\{a'_1, a'_2 \in \mathcal{A} | \omega_{a'_1 a'_2} = 0\}} \left(\sum_{a \in \mathcal{A}} (E_a - E_{a'_2}) \Gamma_0 \frac{a'_1 a'_2}{a a} \right) \\ & \times \langle a'_1 | D_A(\bar{t}) | a'_2 \rangle \\ \equiv & \text{Tr}(\mathcal{S}_A D_A^I(\bar{t})) \end{aligned} \quad (49)$$

with

$$\langle a'_2 | \mathcal{S}_A | a'_1 \rangle = \sum_{a \in \mathcal{A}} (E_a - E_{a'_2}) \Gamma_0 \frac{a'_1 a'_2}{a a}. \quad (50)$$

Adopting the coarse-graining approach for large time intervals described by equation (21) or, equivalently by equation (30), the matrix elements $\langle a'_2 | \mathcal{S}_A | a'_1 \rangle$ are zero for $\omega_{a'_1 a'_2} \neq 0$. The operator \mathcal{S}_A is self-adjoint and commutes with H_A . It describes an energy source or an energy sink provided by the bath. The dynamical influence of the bath is determined by the functions $\chi_{\alpha\beta}(\omega_{a'_1 a'_2})$, which enter the definition (38) of the coefficients $\Gamma_0 \frac{a'_1 a'_2}{a a}$. Starting from equation (32), we introduce the decomposition

$$\chi_{\alpha\beta}(\omega) = \chi'_{\alpha\beta}(\omega) + i \chi''_{\alpha\beta}(\omega)$$

with

$$\chi'_{\alpha\beta}(\omega) \equiv \chi'_{\alpha\beta}(-\omega)^* = \frac{1}{\hbar} \int_{-\infty}^{\infty} \text{Re}(c_{\alpha\beta}(\tau)) e^{i\omega\tau} d\tau \quad (51)$$

and

$$\chi''_{\alpha\beta}(\omega) \equiv \chi''_{\alpha\beta}(-\omega)^* = \frac{1}{\hbar} \int_{-\infty}^{\infty} \text{Im}(c_{\alpha\beta}(\tau)) e^{i\omega\tau} d\tau. \quad (52)$$

From equation (9) we find that the matrices $(\chi'_{\alpha\beta}(\omega))$ and $(\chi''_{\alpha\beta}(\omega))$ are hermitian and anti-hermitian, respectively, i.e.,

$$\begin{aligned} \chi'_{\alpha\beta}(\omega)^* &= \chi'_{\beta\alpha}(\omega), \\ \chi''_{\alpha\beta}(\omega)^* &= -\chi''_{\beta\alpha}(\omega). \end{aligned}$$

Inserting the expression (38) for the coefficients $\Gamma_0 \frac{a'_1 a'_2}{a a}$ into the definition (50), we can rewrite the source term as

$$\mathcal{S}_A = \mathcal{F}_A + \mathcal{D}_A$$

where the matrix elements of the operators \mathcal{F}_A and \mathcal{D}_A are zero for $\omega_{a'_1 a'_2} \neq 0$, and

$$\begin{aligned} \langle a'_2 | \mathcal{F}_A | a'_1 \rangle &= \\ &- \sum_{\alpha, \beta} \sum_{a \in \mathcal{A}} \omega_{a'_1 a} \langle a'_2 | A_\alpha | a \rangle \langle a | A_\beta | a'_1 \rangle \chi'_{\alpha\beta}(\omega_{a'_1 a}) \\ \langle a'_2 | \mathcal{D}_A | a'_1 \rangle &= \\ &- i \sum_{\alpha, \beta} \sum_{a \in \mathcal{A}} \omega_{a'_1 a} \langle a'_2 | A_\alpha | a \rangle \langle a | A_\beta | a'_1 \rangle \chi''_{\alpha\beta}(\omega_{a'_1 a}) \end{aligned}$$

for $\omega_{a'_1 a'_2} = 0$. Clearly, the thus defined operators \mathcal{F}_A and \mathcal{D}_A are self-adjoint and commute with H_A . Equation (49) now becomes

$$\frac{dE_A(\bar{t})}{d\bar{t}} = \text{Tr}(\mathcal{F}_A D_A(\bar{t})) + \text{Tr}(\mathcal{D}_A D_A(\bar{t})). \quad (53)$$

Let us recall that the correlation functions (9), which enter the definitions (51) and (52), describe the dynamical

response of the bath subsystem B to the perturbation by the subsystem A . The real parts are given by

$$\text{Re}(c_{\alpha\beta}(t-t')) = \frac{1}{2} \text{Tr}(\rho_B^0 \{B_\alpha^I(t), B_\beta^I(t')\}),$$

where the symbol $\{\dots, \dots\}$ stands for the anti-commutator. They may be seen as the quantum analog of a classical correlation function. Consequently, the term \mathcal{F}_A may be associated with the contribution of the fluctuations. The operator term \mathcal{D}_A is associated with the imaginary parts of the correlation functions

$$\text{Im}(c_{\alpha\beta}(t-t')) = \frac{1}{2i} \text{Tr}(\rho_B^0 [B_\alpha^I(t), B_\beta^I(t')]).$$

Under certain conditions, which will be discussed in the following, it leads to energy dissipation.

The operator \mathcal{D}_A commutes with H_A . Thus, the eigenvectors of H_A forming the basis set $\{|a\rangle\}$ can be chosen to be simultaneously eigenvectors of \mathcal{D}_A . The eigenvalues of \mathcal{D}_A are given by

$$\begin{aligned} \langle a' | \mathcal{D}_A | a' \rangle &= \\ &- \sum_{\alpha, \beta} \sum_a \langle a' | A_\alpha | a \rangle \langle a | A_\beta | a' \rangle \psi_{\alpha\beta}(\omega_{a'a}) \end{aligned}$$

with

$$\begin{aligned} \psi_{\alpha\beta}(\omega) &= i\omega \chi''_{\alpha\beta}(\omega) \\ &= \frac{\pi}{\hbar} \sum_{b, b'} (p_b - p_{b'}) \omega_{b'b} \langle b | B_\alpha | b' \rangle \langle b' | B_\beta | b \rangle \\ &\quad \times \delta(\omega - \omega_{b'b}). \end{aligned}$$

The last equality is obtained from the definition (52) of $\chi''_{\alpha\beta}(\omega)$ and using equation (34). Obviously, the hermitian matrix $(\psi_{\alpha\beta}(\omega))$ is positive if and only if

$$(p_b - p_{b'}) \omega_{b'b} \geq 0, \quad \forall b, b'.$$

In other words, \mathcal{D}_A is always negative if the bath at statistical equilibrium satisfies the condition

$$E_b \geq E_{b'} \iff p_b \leq p_{b'}, \quad \forall b, b'. \quad (54)$$

When the subsystem A is at equilibrium, the two terms on the right-hand side of equation (53) cancel each other, i.e., the dissipative term $\text{Tr}(\mathcal{D}_A D_A^I(\bar{t}))$ is compensated by the term $\text{Tr}(\mathcal{F}_A D_A^I(\bar{t}))$ associated with the fluctuations. This generalizes the fluctuation-dissipation theorem [33–35] to the case of non-thermal equilibria.

In particular, the condition (54) is satisfied for a thermal bath with a positive temperature T , where

$$p_b = \frac{1}{Z_B} \exp\left(-\frac{E_b}{k_B T}\right).$$

The fluctuation-dissipation theorem then implies

$$\chi''_{\alpha\beta}(\omega) = -i \tanh\left(\frac{\hbar\omega}{2k_B T}\right) \chi'_{\alpha\beta}(\omega). \quad (55)$$

4 Kramers-Kronig relations

In the following we derive the Kramers-Kronig relations for the advanced and retarded susceptibilities corresponding to equation (A.7). We first establish the relations between the functions $\chi_{\alpha\beta}(\omega)$ and $\bar{\chi}_{\alpha\beta}(\omega)$ defined in equations (32, 33), respectively. Starting from the definition of $\bar{\chi}_{\alpha\beta}(\omega)$ in equation (33)

$$\bar{\chi}_{\alpha\beta}(\omega) = \frac{i}{\hbar} \int_{-\infty}^{\infty} \epsilon(\tau) c_{\alpha\beta}(\tau) e^{i\omega\tau} d\tau \quad (56)$$

and rewriting the Heaviside function as

$$\epsilon(\tau) = \lim_{\eta \rightarrow 0} \frac{i}{2\pi} \int_{-\infty}^{\infty} \left(\frac{1}{\omega' + i\eta} + \frac{1}{\omega' - i\eta} \right) e^{-i\omega'\tau} d\omega',$$

we get

$$\begin{aligned} \bar{\chi}_{\alpha\beta}(\omega) &= - \lim_{\eta \rightarrow 0} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} d\tau c_{\alpha\beta}(\tau) \\ &\quad \times \int_{-\infty}^{\infty} d\omega' \left(\frac{1}{\omega' + i\eta} + \frac{1}{\omega' - i\eta} \right) \\ &\quad \times e^{i(\omega - \omega')\tau} \\ &= - \lim_{\eta \rightarrow 0} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \left(\frac{1}{\omega' + i\eta} + \frac{1}{\omega' - i\eta} \right) \\ &\quad \times \chi_{\alpha\beta}(\omega - \omega'), \end{aligned}$$

where we have made use of the definition (32). Finally, changing the integration variable ω' into $\omega - \omega'$, we obtain

$$\bar{\chi}_{\alpha\beta}(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_{\alpha\beta}(\omega')}{\omega - \omega'} d\omega'. \quad (57)$$

Similarly, rewriting the definition (32) of $\chi_{\alpha\beta}(\omega)$ as

$$\chi_{\alpha\beta}(\omega) = \frac{1}{\hbar} \int_{-\infty}^{\infty} \epsilon(\tau) \{ \epsilon(\tau) c_{\alpha\beta}(\tau) \} e^{i\omega\tau} d\tau$$

and otherwise using the same arguments as above, we find

$$\chi_{\alpha\beta}(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\bar{\chi}_{\alpha\beta}(\omega')}{\omega - \omega'} d\omega'. \quad (58)$$

The Hilbert transforms (57) and (58) establish the so-called Kramers-Kronig relations. They are equivalent to the commonly used Kramers-Kronig relations between the real and the imaginary part of the susceptibility functions. In fact, the susceptibility functions $\kappa_{\alpha\beta}^{ret}(\omega)$ and $\kappa_{\alpha\beta}^{adv}(\omega)$ describing the retarded and the advanced response, respectively, are given by the Fourier transforms of the functions

$$\begin{aligned} c_{\alpha\beta}^{ret}(t-t') &= -\frac{i}{\hbar} \text{Tr}(\rho_B^0 [B_{\alpha}^I(t), B_{\beta}^I(t')]) \Theta(t-t') \\ &= \frac{2}{\hbar} \text{Im}(c_{\alpha\beta}(t-t')) \Theta(t-t') \end{aligned} \quad (59)$$

and

$$\begin{aligned} c_{\alpha\beta}^{adv}(t-t') &= -\frac{i}{\hbar} \text{Tr}(\rho_B^0 [B_{\alpha}^I(t), B_{\beta}^I(t')]) \Theta(t'-t) \\ &= \frac{2}{\hbar} \text{Im}(c_{\alpha\beta}(t-t')) \Theta(t'-t) \end{aligned} \quad (60)$$

with

$$\Theta(\tau) = \begin{cases} 0 & \text{if } \tau < 0 \\ \frac{1}{2} & \text{if } \tau = 0 \\ 1 & \text{if } \tau > 0. \end{cases}$$

We first consider the retarded response. According to equation (59) we can write

$$c_{\alpha\beta}^{ret}(\tau) = \frac{1}{\hbar} (\text{Im}(c_{\alpha\beta}(\tau)) + \epsilon(\tau) \text{Im}(c_{\alpha\beta}(\tau))).$$

The Fourier transform $\kappa_{\alpha\beta}^{ret}(\omega)$ of the above function can be expressed in the form

$$\kappa_{\alpha\beta}^{ret}(\omega) = \chi_{\alpha\beta}''(\omega) - i\bar{\chi}_{\alpha\beta}''(\omega), \quad (61)$$

where the function $\chi_{\alpha\beta}''(\omega)$ is defined by equation (52), and

$$\bar{\chi}_{\alpha\beta}''(\omega) = \frac{1}{\hbar} \int_{-\infty}^{\infty} \epsilon(\tau) \text{Im}(c_{\alpha\beta}(\tau)) e^{i\omega\tau} d\tau. \quad (62)$$

Starting from equation (60) and otherwise following the same arguments, we obtain for the susceptibility function corresponding to the advanced response

$$\kappa_{\alpha\beta}^{adv}(\omega) = \chi_{\alpha\beta}''(\omega) + i\bar{\chi}_{\alpha\beta}''(\omega), \quad (63)$$

Now, it can easily be seen that the above derivation of the Kramers-Kronig relations (57) and (58) remains valid when we replace $c_{\alpha\beta}(\tau)$ in equation (56) by $\text{Im}(c_{\alpha\beta}(\tau))$. This means that the Kramers-Kronig relations (57) and (58) hold likewise for $\chi_{\alpha\beta}''(\omega)$ and $\bar{\chi}_{\alpha\beta}''(\omega)$. Using these relations we find immediately

$$\begin{aligned} \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_{\alpha\beta}''(\omega') \mp i\bar{\chi}_{\alpha\beta}''(\omega')}{\omega - \omega'} d\omega' = \\ -i(\pm\chi_{\alpha\beta}''(\omega) - i\bar{\chi}_{\alpha\beta}''(\omega)). \end{aligned}$$

From equations (61, 63), we then get

$$\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\kappa_{\alpha\beta}^{ret}(\omega')}{\omega - \omega'} d\omega' = -i\kappa_{\alpha\beta}^{ret}(\omega)$$

and

$$\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\kappa_{\alpha\beta}^{adv}(\omega')}{\omega - \omega'} d\omega' = i\kappa_{\alpha\beta}^{adv}(\omega).$$

Taking the real or the imaginary part of the above equation, we obtain the usual form of the Kramers-Kronig relations for the susceptibility functions describing either the retarded or the advanced response.

5 Stationary response to an external time-periodic perturbation

In the following we will apply our approach to study the stationary properties of the “bathed” subsystem A in presence of an external time-periodic perturbation. We describe the perturbation by an extra term $H_{\text{ext}}(t)$ added to the Hamiltonian H_A . We will assume that the perturbation does neither affect the equilibrium statistical state of the bath nor the dynamical coupling of the bath B to the subsystem A .

Clearly, to treat this problem it is appropriate to adopt the Schrödinger picture. We first define the Liouville superoperator L

$$L(X) = \Gamma(X) + L_H(X), \quad \forall X \in \mathcal{L}(\mathcal{H}_A), \quad (64)$$

where the superoperator Γ is defined by equation (28), and

$$L_H(X) = \frac{i}{\hbar} [X, H_A], \quad \forall X \in \mathcal{L}(\mathcal{H}_A). \quad (65)$$

Referring to the Hilbert-Schmidt scalar product

$$\langle X | Y \rangle = \text{Tr}(X^\dagger Y), \quad X, Y \in \mathcal{L}(\mathcal{H}_A), \quad (66)$$

the linear superoperator L_H is “anti-selfadjoint”,

$$L_H^\dagger = -L_H.$$

Starting from the definitions (28), (64) and (65), it is easily shown that

$$L_H(X^\dagger) = (L_H(X))^\dagger, \quad (67)$$

$$\Gamma(X^\dagger) = (\Gamma(X))^\dagger, \quad (68)$$

$$L(X^\dagger) = (L(X))^\dagger. \quad (69)$$

In order to simplify the notation, we will from now on denote the coarse-grained density matrix D_A by D . The equation of evolution (27), including the contribution of the Hamiltonian term $H_{\text{ext}}(t)$, then becomes

$$\frac{dD(t)}{dt} = L(D(t)) + \frac{i}{\hbar} [D(t), H_{\text{ext}}(t)] \quad (70)$$

with $\text{Tr}(D) = 1$. The time-periodic perturbation will be taken as

$$H_{\text{ext}}(t) = F_A e^{-i\omega t} + F_A^\dagger e^{i\omega t}. \quad (71)$$

Clearly, equation (70) makes sense only if the change of the perturbation $H_{\text{ext}}(t)$ is negligible over times of the order of the coarse graining time. We will therefore assume that

$$2\pi/\omega \gg \Delta t \gg \tau_B^{\text{corr}}.$$

Moreover, in order to reveal resonance features, the chosen frequency ω should be of the order of the transition

frequencies $\omega_{aa'}$ of the subsystem A . Multiplying the perturbation $H_{\text{ext}}(t)$ by the parameter λ with $0 \leq \lambda \leq 1$, we get from equations (70, 71)

$$\begin{aligned} \frac{dD(t)}{dt} = L(D(t)) + \frac{i\lambda}{\hbar} [D(t), F_A] e^{-i\omega t} \\ + \frac{i\lambda}{\hbar} [D(t), F_A^\dagger] e^{i\omega t}. \end{aligned} \quad (72)$$

The solution for the time-averaged density matrix can be written as a power series with respect to the parameter λ ,

$$D(t) = \sum_{n=0}^{\infty} \lambda^n D_n(t) \quad (73)$$

with

$$\begin{aligned} \text{Tr}(D_0) &= 1, \\ \text{Tr}(D_n(t)) &= 0, \quad \forall n > 0, \forall t, \\ D_n^\dagger(t) &= D_n(t), \quad \forall n, \forall t. \end{aligned}$$

Inserting the expression (73) into equation (72) and equating λ^n terms on both sides, we get

$$\begin{aligned} \frac{dD_n(t)}{dt} = L(D_n(t)) + \frac{i}{\hbar} [D_{n-1}(t), F_A] e^{-i\omega t} \\ + \frac{i}{\hbar} [D_{n-1}(t), F_A^\dagger] e^{i\omega t}. \end{aligned} \quad (74)$$

The solution D_0 for $\lambda = 0$ describes the coarse-grained density matrix in absence of the external perturbation. Being time-independent, it satisfies the relation

$$L(D_0) = 0. \quad (75)$$

For the following discussion we will assume that the unperturbed solution D_0 is unique. Making use of Floquet's theorem [36], we obtain for the stationary solutions

$$D_n(t) = \sum_{k=-n}^n D_n^k e^{ik\omega t} \quad (76)$$

with

$$D_0^0 \equiv D_0 \quad (77)$$

and

$$\begin{aligned} \text{Tr}(D_0^0) &= 1, \\ \text{Tr}(D_n^k) &= 0, \quad \forall n > 0, \\ D_n^{-k} &= D_n^{k\dagger}, \quad |k| \leq n. \end{aligned}$$

The property

$$D_n^k = 0 \quad \text{for } |k| > n, \quad (78)$$

leading to the limitation of the summation in equation (76), follows from the fact that the recursion starts

from the time-independent D_0 . Inserting equation (76) into equation (74), we obtain the recursion relation

$$(ik\omega - L) D_n^k = \frac{i}{\hbar} [D_{n-1}^{k+1}, F_A] + \frac{i}{\hbar} [D_{n-1}^{k-1}, F_A^\dagger]. \quad (79)$$

From the condition (78) we find

$$L(D_1^0) = 0, \quad (80)$$

i.e., D_1^0 satisfies the same relation as D_0 (see Eq. (75)). Since presently we have assumed that equation (75) possesses a unique solution, only the trivial solution of equation (80) is admissible, i.e.,

$$D_1^0 = 0.$$

From the condition (78) and the relations (79) we then find that

$$D_n^{n-1} = 0, \quad \forall n > 0.$$

Following the same arguments, it is easy to see that

$$D_n^k = 0, \quad \text{for odd } |n - k|.$$

Expressed in terms of the linear superoperators

$$R_-(z) X = \frac{1}{\hbar} \frac{\mathbf{1}}{z\mathbf{1} + iL} [X, F_A], \quad (81)$$

$$R_+(z) X = \frac{1}{\hbar} \frac{\mathbf{1}}{z\mathbf{1} + iL} [X, F_A^\dagger], \quad (82)$$

$$(R_-(z) X)^\dagger = R_+(-z) X^\dagger, \quad (83)$$

where the last relation follows directly from the preceding definitions and the property (69), the recursion relations (79) become

$$D_n^k = R_-(k\omega) D_{n-1}^{k+1} + R_+(k\omega) D_{n-1}^{k-1}. \quad (84)$$

This relation can be used to express the solutions D_n^k in terms of the zero-field solution D_0 (77).

The recurrence relations show that high-frequency contributions correspond to high-order perturbation terms. A stationary solution exists only if the series (73) converges for $\lambda = 1$. We thus may assume in the following that the terms D_n^k become negligible for $|k| > k_m$. Then, the recursion relations can be formally written in the compact form

$$Q_n = T^n Q_0, \quad (85)$$

where T is a tridiagonal $(2k_m + 1) \times (2k_m + 1)$ matrix with the elements

$$T_{k,l} = \begin{cases} R_+(k\omega) & \text{for } l = k - 1, \\ & k = k_m, \dots, -k_m + 1 \\ R_-(k\omega) & \text{for } l = k + 1, \\ & k = k_m - 1, \dots, -k_m \\ 0 & \text{otherwise} \end{cases}$$

with $k, l = k_m, \dots, -k_m$, and the column vectors

$$Q_0 = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ D_0^0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad Q_n = \begin{pmatrix} D_n^{k_m} \\ \vdots \\ D_n^0 \\ \vdots \\ D_n^{-k_m} \end{pmatrix}.$$

For the evaluation of the recursion relations (85) it is convenient to express the operators H_A and F_A in an operator basis, and then to study the action of the superoperators L, L_H and Γ on these basis operators. In the following we assume that the eigenstates of H_A are non-degenerate, and that they are labeled such that

$$E_a - E_{a'} > 0, \quad a, a' = 1, \dots, N \quad \text{for } a > a'.$$

A state $|a\rangle$ may be associated with the vector

$$e_a = (0, \dots, 0, 1, 0, \dots, 0), \quad e_a \in \tilde{\mathbb{R}}^N$$

where the 1 is placed at the a -th position. Then the vectors

$$\alpha = e_a - e_{a'} = (0, \dots, 0, -1, 0, \dots, 0, 1, 0, \dots, 0) \\ = (\alpha_1, \dots, \alpha_N)$$

identify pairs of coupled states $|a\rangle$ and $|a'\rangle$. The set of vectors α will be denoted \mathcal{R} . Using this notation, we define the operators

$$P_a = |a\rangle\langle a|, \quad a = 1, \dots, N.$$

and

$$X_\alpha = |a\rangle\langle a'|, \quad a \neq a', \quad a, a' = 1, \dots, N. \quad (86)$$

Obviously, we have

$$P_a^\dagger = P_a, \quad X_\alpha^\dagger = X_{-\alpha}. \quad (87)$$

The operators P_a and X_α form an orthonormal basis with respect to the Hilbert-Schmidt scalar product (see Eq. (66)),

$$\langle X_\alpha | X_\beta \rangle = \delta_{\alpha\beta}, \\ \langle P_a | P_{a'} \rangle = \delta_{aa'}, \\ \langle X_\alpha | P_a \rangle = 0. \quad (88)$$

They satisfy the commutation relations

$$[P_a, P_{a'}] = 0, \quad (89)$$

$$[X_\alpha, X_\beta] = c_{\alpha\beta}^\gamma X_\gamma, \quad \alpha, \beta \in \mathcal{R}, \alpha + \beta \neq 0, \quad (90)$$

$$[X_\alpha, X_{-\alpha}] = \sum_{a=1}^N \alpha_a P_a = \alpha \cdot P, \quad (91)$$

with

$$c_{\alpha\beta}^\gamma = \begin{cases} +1 & \text{if } \gamma = \alpha - \beta \in \mathcal{R} \\ -1 & \text{if } \gamma = \alpha + \beta \in \mathcal{R} \\ 0 & \text{otherwise} \end{cases} \quad (92)$$

and

$$P = (P_1, \dots, P_N).$$

For an operator

$$Y = y \cdot P, \quad y \in \mathbb{C}^N$$

with

$$y = (y_1, \dots, y_N)$$

we obtain

$$[Y, X_\beta] = (y \cdot \beta) X_\beta \quad (93)$$

Defining the vector

$$E = (E_1, E_2, \dots, E_N),$$

where $E_i, i = 1, \dots, N$ denote the state energies of the considered N-level system, we get for the transition frequency associated with X_α

$$\omega_\alpha = \omega_{aa'} = \frac{1}{\hbar} \alpha \cdot E.$$

Expressed in this operator basis, the Hamiltonian H_A reads

$$H_A = \sum_{a=1}^N E_a P_a = E \cdot P.$$

According to equations (89, 93) it satisfies the commutation relations

$$[H_A, Y] = 0, \quad (94)$$

$$[H_A, X_\alpha] = (E \cdot \alpha) X_\alpha. \quad (95)$$

The operator F_A entering the definition of the perturbation term in equation (71) can be written

$$F_A = \sum_{\alpha} f_{\alpha} X_{\alpha}, \quad f_{\alpha} \in \mathbb{C}, \forall \alpha \in \mathcal{R}. \quad (96)$$

Equations (94, 95) allow us to describe the action of the superoperators L_H, L and Γ on the basis operators. For the Liouville operator L_H we obtain

$$L_H(P_a) = 0, \quad (97)$$

$$L_H(X_\alpha) = -i \omega_\alpha X_\alpha. \quad (98)$$

The superoperator Γ describes the weak interaction of the subsystem A with the bath. In the following we will assume that the corresponding coupling between the operator subspaces spanned by $P_b, b = 1, \dots, N$ and $X_\alpha, \alpha \in \mathcal{R}$ is negligible, so that

$$\begin{aligned} \langle X_\alpha | \Gamma(P_b) \rangle &= \Gamma_{a a'}^{b b} \simeq 0, \\ \langle P_b | \Gamma(X_\alpha) \rangle &= \Gamma_{b b}^{a a'} \simeq 0. \end{aligned} \quad (99)$$

Looking for the Markovian coarse-grained evolution, the situation is adequately treated using the convention (30). In this case, the above conditions are immediately valid for the presently discussed situation of a non-degenerate excitation spectrum. Even for the non-Markovian regime on shorter time-scales covered by the Redfield equations (see Eqs. (18, 20)) the approximation (99) will be appropriate in many situations.

The action of the superoperator Γ in the operator subspace spanned by the operators X_α can be treated in first-order perturbation theory if the associated transition frequencies $\hbar\omega_\alpha$ are not too small. Under this assumption, we can neglect the non-diagonal matrix elements

$$\langle X_\alpha | \Gamma(X_\beta) \rangle, \quad \alpha \neq \beta$$

and put

$$\Gamma(X_\alpha) = -\lambda_\alpha X_\alpha \quad \text{with} \quad \lambda_\alpha = -\Gamma_{aa'}^{aa'}. \quad (100)$$

According to equation (40), we have $\text{Re}(\lambda_\alpha) \geq 0$. For the here considered systems possessing a unique solution of equation (75) we have even

$$\text{Re}(\lambda_\alpha) > 0, \quad (101)$$

since otherwise excitations of type α cannot relax. From equations (98) and (100), we get

$$L(X_\alpha) = -i \Omega_\alpha X_\alpha \quad \text{with} \quad \Omega_\alpha = \omega_\alpha - i\lambda_\alpha, \quad (102)$$

i.e., treating the operator Γ in first-order perturbation theory, the basis vectors X_α become eigenstates of the operator L . From equations (87) and (69) it follows that

$$\Omega_{-\alpha} = -\Omega_\alpha^*.$$

The action of the superoperator Γ in the operator subspace spanned by the projectors P_a has to be considered with some more care. The matrix elements of Γ in this subspace are given by

$$\langle P_a | \Gamma(P_{a'}) \rangle = \Gamma_{aa'}^{a'a'}.$$

From equation (44) we see that the diagonal and non-diagonal matrix elements of the operator Γ are of the same order. According to equation (97) the operator L_H does not contribute to the eigenvalues of L . Thus, the diagonal and off-diagonal elements of L being of the same order, we are now obliged to solve the eigenvalue problem for the operator Γ in this subspace. In order to avoid unnecessary complications, we will assume in the following that the eigenvalues of L in the operator subspace spanned by the operators $P_a, a = 1, \dots, N$ are all different. Then, apart from the solution $Y_0 (= D_0)$ corresponding to the eigenvalue zero, we have further N-1 non-orthogonal eigenstates Y_l satisfying the equation

$$L(Y_l) = -i\Omega_l Y_l, \quad l = 1, \dots, N-1, \quad (103)$$

with $\Omega_l \neq 0$ and, since $\text{Tr}(\Gamma(P_a)) = 0, \forall a$,

$$\text{Tr}(Y_l) = 0, \quad l = 1, \dots, N-1. \quad (104)$$

The eigenstates

$$Y_l = \sum_{a=1}^N y_{la} P_a = y_l \cdot P, \quad l = 1, \dots, N-1 \quad (105)$$

may be normalized. They are, however, non-orthogonal, so we have

$$\text{Tr} \left(Y_{l'}^\dagger Y_l \right) = \sum_{a=1}^N y_{l'a}^* y_{la} \equiv g_{l'l}, \quad g_{ll} = 1. \quad (106)$$

From equation (93) we find immediately

$$\begin{aligned} [Y_l, X_\alpha] &= (y_l \cdot \alpha) X_\alpha \\ &\equiv c_{l\alpha}^\alpha X_\alpha \end{aligned} \quad (107)$$

for $l = 1, \dots, N-1$, $\alpha \in \mathcal{R}$. Similarly, writing the normalized equilibrium solution as

$$Y_0 = y_0 \cdot P,$$

we get

$$\begin{aligned} [Y_0, X_\alpha] &= (y_0 \cdot \alpha) X_\alpha \\ &\equiv p_{0\alpha} X_\alpha. \end{aligned} \quad (108)$$

The presumed stability of the system in the neighborhood of its equilibrium density matrix D_0 requires that the real parts of the eigenvalues $-i\Omega_l$ are all negative. This property follows directly from the relations (23), (39), (44) and Gerschgorin's theorem [37].

For the following discussion it is convenient to decompose the superoperators $R_-(z)$ and $R_+(z)$ defined in equations (81, 82). We thus write

$$R_-(z) = \sum_{\beta \in \mathcal{R}} f_\beta R_\beta(z), \quad (109)$$

$$R_+(z) = \sum_{\beta \in \mathcal{R}} f_{-\beta}^* R_\beta(z) \quad (110)$$

with

$$R_\beta(z) X = \frac{1}{\hbar} \frac{\mathbf{1}}{z\mathbf{1} + iL} [X, X_\beta]. \quad (111)$$

The action of the operators $R_\beta(z)$ on the operators X_α and Y_l is obtained from equations (90, 102, 91). We find

$$R_\beta(z) X_\alpha = \frac{1}{\hbar} \frac{\mathbf{1}}{z\mathbf{1} + iL} \begin{cases} c_{\alpha\beta}^\gamma X_\gamma, & \gamma = \alpha \pm \beta \in \mathcal{R} \\ \sum_{l=1}^{N-1} c_{\alpha, -\alpha}^l Y_l, & \beta = -\alpha \\ 0 & \text{otherwise,} \end{cases} \quad (112)$$

where the coefficients $c_{\alpha, -\alpha}^l$ are obtained from equations (91, 105, 106),

$$c_{\alpha, -\alpha}^l = \alpha \cdot \left(\sum_{l'=1}^{N-1} (g^{-1})_{ll'} y_{l'} \right), \quad l = 1, \dots, N-1.$$

Equation (112) can be evaluated using equations (102, 103),

$$R_\beta(z) X_\alpha = \begin{cases} \frac{1}{\hbar} \frac{c_{\alpha\beta}^\gamma}{z + \Omega_\gamma} X_\gamma, & \gamma = \alpha \pm \beta \in \mathcal{R} \\ \frac{1}{\hbar} \sum_{l=1}^{N-1} \frac{c_{\alpha, -\alpha}^l}{z + \Omega_l} Y_l, & \beta = -\alpha \\ 0, & \text{otherwise.} \end{cases} \quad (113)$$

Similarly, we get from equations (111, 102, 107)

$$\begin{aligned} R_\beta(z) Y_l &= \frac{1}{\hbar} \frac{\mathbf{1}}{z\mathbf{1} + iL} [Y_l, X_\beta] \\ &= \frac{1}{\hbar} \frac{c_{l\beta}^\beta}{z + \Omega_\beta} X_\beta, \quad l = 1, \dots, N-1. \end{aligned} \quad (114)$$

With the decompositions (109) and (110) the recursion relations (84) become

$$D_n^k = \sum_{\beta \in \mathcal{R}} f_\beta R_\beta(k\omega) D_{n-1}^{k+1} + f_{-\beta}^* R_\beta(k\omega) D_{n-1}^{k-1}. \quad (115)$$

For $n \geq 1$ the operators D_n^k can be expressed in terms of the operators X_α , $\alpha \in \mathcal{R}$ and Y_l , $l = 1, \dots, N-1$,

$$D_n^k = \sum_{\beta \in \mathcal{R}} x_{n\beta}^k X_\beta + \sum_{l=1}^{N-1} y_{nl}^k Y_l. \quad (116)$$

From the first recursion step and equation (108), we obtain

$$y_{nl}^k = 0, \quad l = 1, \dots, N, \quad k = -k_m, \dots, k_m \quad (117)$$

and

$$x_{1\alpha}^k = \begin{cases} \frac{1}{\hbar} \frac{f_{-\alpha}^* p_{0\alpha}}{\omega + \Omega_\alpha}, & k = 1, \quad \alpha \in \mathcal{R} \\ \frac{1}{\hbar} \frac{f_\alpha p_{0\alpha}}{-\omega + \Omega_\alpha}, & k = -1, \quad \alpha \in \mathcal{R} \\ 0 & \text{otherwise.} \end{cases} \quad (118)$$

For convenience, we now combine the coefficients $x_{n\alpha}^k$, $\alpha \in \mathcal{R}$ and y_{nl}^k , $l = 1, \dots, N-1$ into column vectors x_n^k and y_n^k . After insertion of the decomposition (116) into the recursion relations (115) and making use of equations (88, 106) we then get for $n \geq 2$,

$$\begin{aligned} \begin{pmatrix} x_n^k \\ y_n^k \end{pmatrix} &= \begin{pmatrix} A_+^k(\omega) & B_+^k(\omega) \\ C_+^k(\omega) & 0 \end{pmatrix} \begin{pmatrix} x_{n-1}^{k+1} \\ y_{n-1}^{k+1} \end{pmatrix} \\ &+ \begin{pmatrix} A_-^k(\omega) & B_-^k(\omega) \\ C_-^k(\omega) & 0 \end{pmatrix} \begin{pmatrix} x_{n-1}^{k-1} \\ y_{n-1}^{k-1} \end{pmatrix}. \end{aligned} \quad (119)$$

The matrix elements of the matrices $A_\pm^k(\omega)$, $B_\pm^k(\omega)$ and $C_\pm^k(\omega)$ are obtained from equations (112, 113, 114).

Making also use of the definition (92) we get

$$\begin{aligned}
(A_+^k(\omega))_{\alpha\beta} &= \begin{cases} \frac{1}{\hbar} \frac{1}{k\omega + \Omega_\alpha} (f_{\beta-\alpha} - f_{\alpha-\beta}), & \alpha - \beta \in \mathcal{R} \\ 0 & \text{otherwise} \end{cases} \\
(A_-^k(\omega))_{\alpha\beta} &= \begin{cases} \frac{1}{\hbar} \frac{1}{k\omega + \Omega_\alpha} (f_{\alpha-\beta}^* - f_{\beta-\alpha}^*), & \alpha - \beta \in \mathcal{R} \\ 0 & \text{otherwise} \end{cases} \\
(B_+^k(\omega))_{\alpha l} &= \frac{f_\alpha}{\hbar} \frac{c_{l\alpha}^\alpha}{k\omega + \Omega_\alpha}, \\
(B_-^k(\omega))_{\alpha l} &= \frac{f_{-\alpha}^*}{\hbar} \frac{c_{l\alpha}^\alpha}{k\omega + \Omega_\alpha}, \\
(C_+^k(\omega))_{l\alpha} &= \frac{f_{-\alpha}}{\hbar} \frac{c_{\alpha,-\alpha}^l}{k\omega + \Omega_l}, \\
(C_-^k(\omega))_{l\alpha} &= \frac{f_\alpha^*}{\hbar} \frac{c_{\alpha,-\alpha}^l}{k\omega + \Omega_l}
\end{aligned} \tag{120}$$

for $\alpha, \beta \in \mathcal{R}$ and $l = 1, \dots, N - 1$. From equations (119, 120) we expect resonant behavior of the populations and the coherences at frequencies $\omega = \omega_\alpha/k$, $k = \pm 1, \pm 2, \dots$

The population terms y_n^k are generated by the coherence terms x_{n-1}^{k+1} and x_{n-1}^{k-1} ,

$$y_n^k = C_+^k(\omega) x_{n-1}^{k+1} + C_-^k(\omega) x_{n-1}^{k-1}. \tag{121}$$

From equation (119) and using the above identity we obtain a recursion relation for the coherences

$$\begin{aligned}
x_n^k &= A_+^k(\omega) x_{n-1}^{k+1} + B_+^k(\omega) C_+^{k+1}(\omega) x_{n-2}^{k+2} \\
&+ B_+^k(\omega) C_-^{k+1}(\omega) x_{n-2}^k + A_-^k(\omega) x_{n-1}^{k-1} \\
&+ B_-^k(\omega) C_+^{k-1}(\omega) x_{n-2}^k + B_-^k(\omega) C_-^{k-1}(\omega) x_{n-2}^{k-2},
\end{aligned} \tag{122}$$

where the starting term is given by equation (118). In terms of the column vectors

$$x_n = \begin{pmatrix} x_n^{k_m} \\ \vdots \\ x_n^{-k_m} \end{pmatrix} \tag{123}$$

the solutions of equation (122) may be written in the compact form

$$\begin{pmatrix} x_{n+1} \\ x_n \end{pmatrix} = \begin{pmatrix} U & V \\ 1 & 0 \end{pmatrix}^n \begin{pmatrix} x_1 \\ 0 \end{pmatrix} \quad n = 0, 1, 2, \dots,$$

where the matrices U and V are composed of the block-submatrices $U_{kk'}$ and $V_{kk'}$ defined by

$$\begin{aligned}
U_{kk'} &= A_+^k(\omega) \delta_{k'k+1} + A_-^k(\omega) \delta_{k'k-1} \\
V_{kk'} &= B_+^k(\omega) C_+^{k+1}(\omega) \delta_{k'k+2} \\
&+ B_+^k(\omega) C_-^{k+1}(\omega) \delta_{k'k} \\
&+ B_-^k(\omega) C_+^{k-1}(\omega) \delta_{k'k} \\
&+ B_-^k(\omega) C_-^{k-1}(\omega) \delta_{k'k-2}, \quad |k|, |k'| \leq k_m.
\end{aligned}$$

The perturbation series for the coherences can be summed up explicitly. Putting

$$Z = \begin{pmatrix} U & V \\ 1 & 0 \end{pmatrix} \tag{124}$$

we first introduce the sum

$$G_m = \sum_{n=1}^m Z^n,$$

which accounts for the contributions up to m-th order in the perturbation. Then, using the identity

$$(1 - Z)(Z + Z^2 + \dots + Z^m) = Z - Z^{m+1}$$

we obtain the relation

$$(1 - Z)G_m = Z - Z^{m+1}.$$

For sufficiently small perturbations we have

$$Z^m \rightarrow 0 \quad \text{for} \quad m \rightarrow \infty. \tag{125}$$

In this case the matrix $(1 - Z)$ can be inverted, so that

$$\begin{aligned}
G &\equiv \lim_{m \rightarrow \infty} G_m \\
&= (1 - Z)^{-1} Z - \lim_{m \rightarrow \infty} (1 - Z)^{-1} Z^{m+1} \\
&= (1 - Z)^{-1} Z.
\end{aligned}$$

From the definition (124) we obtain immediately

$$(1 - Z)^{-1} = \begin{pmatrix} W & WV \\ W & 1 + WV \end{pmatrix}$$

with

$$W = (1 - U - V)^{-1},$$

and consequently

$$G = \begin{pmatrix} W(U + V) & WV \\ 1 + W(U + V) & WV \end{pmatrix},$$

$$G \begin{pmatrix} x_1 \\ 0 \end{pmatrix} = \begin{pmatrix} W(U + V)x_1 \\ (1 + W(U + V))x_1 \end{pmatrix}.$$

The last relation allows us to write the general solution for the coefficients defining the coherences in the compact form

$$\begin{aligned} x &= \sum_{n=1}^{\infty} x_n \\ &= x_1 + (1 - U - V)^{-1}(U + V) x_1 \\ &= (1 - (U + V))^{-1} x_1. \end{aligned} \quad (126)$$

The start vector x_1 specifying the coherences to first order is given by equation (118).

The coefficients corresponding to the populations are obtained from equation (121). We find

$$\begin{aligned} y &= y_0 + \sum_{n=2}^{\infty} y_n \\ &= y_0 + \tilde{C} (1 - (U + V))^{-1} x_1 \end{aligned} \quad (127)$$

with

$$\tilde{C}_{kk'} = C_+^k(\omega) \delta_{k'k+1} + C_-^k(\omega) \delta_{k'k-1}, \quad |k|, |k'| \leq k_m.$$

The column vectors x and y determine the stationary solution for the density matrix, which is given by equation (73) for $\lambda = 1$. In order to see this, let us recall that the vectors x_n and y_n in equations (126, 127) are composed of the coefficients $x_{n\alpha}^k$ and $y_{n\alpha}^k$, respectively (see Eq. (123)). According to equations (116, 76), they define the n th order contributions $D_n(t)$. Summation over all orders yields the solution (73).

In order to illustrate the above results, we consider a two-level system. In this case, the Γ coefficients describing the effect of the bath are $\Gamma_{11}^{11} = -\Gamma_{22}^{11}$, $\Gamma_{22}^{22} = -\Gamma_{11}^{22}$, and $\Gamma_{12}^{12} = \Gamma_{21}^{21*}$. Assuming a thermal bath we further have $\Gamma_{22}^{11}/\Gamma_{11}^{22} = \exp((E_1 - E_2)/k_B T)$. The coupling to the bath for a given temperature may thus be described by the three free parameters Γ_{11}^{11} , Γ_{22}^{22} and Γ_{12}^{12} . The coefficients f_α determining the time-periodic perturbation (96) are chosen as $f_1 = f_2 \equiv f \in \mathbb{R}$. It can easily be seen that in a two-level system the matrices $A_-^k(\omega)$, $A_+^k(\omega)$ and therefore the matrix U vanish. This is a direct consequence of the fact that there exist no $\alpha, \beta \in \mathcal{R}$ with $\alpha - \beta \in \mathcal{R}$. This feature implies that the coefficients

$$y^k = \sum_{n=1}^{\infty} y_n^k$$

become strictly zero for $k = \pm 1, \pm 3, \pm 5, \dots$. The remaining coefficients $y^k, k = 0, \pm 2, \pm 4, \dots$ show the expected resonant behavior near $\omega = \omega_0/q, q = 1, 3, 5, \dots$ with $\omega_0 = (E_2 - E_1)/\hbar$. An example is given in Figure 1, where we present the frequency dependence of the absolute value of the coefficients

$$y^k = \sum_{n=1}^{\infty} y_n^k$$

for $k = 4$. We find two well-resolved resonances corresponding to $q = 1, 3$. Similar resonance behavior at the

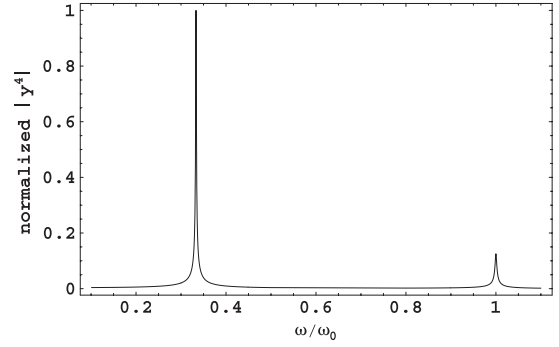


Fig. 1. Absolute value of y^4 representing the fourth-order harmonics of the population as a function of the frequency ω of the external perturbation for a two-level system. The frequency is measured in units of $\omega_0 = (E_2 - E_1)/\hbar$. The response $|y^4|$ is normalized to its maximum value at $\omega = 1/3\omega_0$. The calculated curve was obtained for the parameters $\Gamma_{11}^{11} = -2 \times 10^{-7}$, $\Gamma_{12}^{12} = -2 \times 10^{-3}$, $k_B T = (E_2 - E_1)/10$, and $f = 5 \times 10^{-4}$ (see text).

same frequencies is found for the coefficients

$$x^k = \sum_{n=1}^{\infty} x_n^k,$$

which determine the coherences, the essential difference being that, contrary to the y^k coefficients, the coefficients x^k vanish for $k = \pm 2, \pm 4, \pm 6, \dots$, but they are nonzero for $k = \pm 1, \pm 3, \pm 5, \dots$

For large amplitudes f_α of the external perturbation the condition (125) can no longer be satisfied, and the series (126) and (127) will diverge. Such a behavior indicates that the system is unstable under the influence of the external field. The convergence criterion can be expressed more precisely in terms of the norm of the matrix Z , which is defined as

$$\|Z\| = \sup_x |Zx|, \quad \forall x \quad \text{with } |x| = 1.$$

This norm depends on the parameters characterizing the external perturbation. Multiplying the perturbation term H_{ext} by a factor λ , it is proportional to λ . The convergence of the perturbation series and, correspondingly, the stability of the subsystem A under the influence of the time-periodic perturbation is ensured as long as $\lim_{k_m \rightarrow \infty} \|Z\| <$

1. Following the above defined trajectories in the parameter space starting from arbitrary initial f_α values and frequencies ω , we get all possible stationary solutions.

6 Conclusion

We have derived the master equations describing the evolution of a statistical ensemble of quantum systems weakly coupled to a bath under the most general conditions. Our goal was to achieve a transparent but nevertheless rigorous understanding of the evolution of bathed systems, without making any premature reference to a specific

physical context. Furthermore, we have discussed the non-linear response of the bathed system to an external time-periodic perturbation. In contrast with current standard treatments, we have taken care to avoid any unnecessarily restrictive hypotheses. In particular, the present approach does not rely on the assumption of a bath at “thermal” equilibrium. Thus, the derived Redfield equations (18), the coarse-grained master equations (21) and the relations (23) to (33) for the coefficients $I_{a_1 a_2}^{a_1' a_2'}$ hold for arbitrary statistical equilibrium states of the bath.

The present approach reveals the physical concepts, which are fundamental for any quantum-statistical approach. The most salient feature of open systems embedded in their statistical environment is the gradual loss of memory, which is a necessary prerequisite for any reproducible experiment. The memory loss in the bathed system is introduced via the postulated finite memory of the bath that is quantified by the finite correlation time τ_B^{corr} . This correlation time τ_B^{corr} enters the definition of the correlation functions $c_{\alpha\beta}(\tau)$ (9). The introduction of τ_B^{corr} enables us to restrict the subsequent discussion to the evolution of *finite* subsystems A and B . The approximation (6), consisting of the replacement of the true history by a fictitious one, is the crucial starting point for the subsequent theoretical development. It allows us to get rid of the irrelevant part of the history of the considered system. The properties of the environment are accounted for via the parameters characterizing the finite bath subsystem B , i.e., the correlation functions (9) and the statistical equilibrium state ρ_B^0 . The central role of the correlation functions is clearly revealed by our approach. They determine the functions $\chi_{\alpha\beta}(\omega)$ and $\bar{\chi}_{\alpha\beta}(\omega)$ defined by the Fourier transforms (32) and (33), which in turn determine the coefficients $I_{a_1 a_2}^{a_1' a_2'}$ (see Eqs. (23) to (33)) in the master equations (20, 21). The functions $\chi'_{\alpha\beta}(\omega)$ and $\chi''_{\alpha\beta}(\omega)$ defined in equations (51, 52) are also directly connected with the correlation functions. These functions are useful to separate the dissipative part in the evolution of energy of the bathed system from the part corresponding to energy fluctuations that are due to the interaction of the bathed system with the bath. We derive the so-called fluctuation-dissipation theorem which states that at equilibrium both parts cancel each other. In the particular case of a bath at thermal equilibrium, the functions $\chi'_{\alpha\beta}(\omega)$ and $\chi''_{\alpha\beta}(\omega)$ are related by equation (55). The correlation functions characterizing the bath system determine also the functions $\kappa_{\alpha\beta}^{\text{ret}}(\omega)$ and $\kappa_{\alpha\beta}^{\text{adv}}(\omega)$ describing its linear response, which are defined in equations (61, 63). The respective relations are expressed in terms of the Fourier transforms equations (52, 62), which take care of the causality condition. The Kramers-Kronig relations for both linear response functions, which are discussed in Section 4, are a direct consequence of the definitions (32), (33) and (59).

Most experiments investigate the response of a bathed system to an external perturbation. This situation is illustrated in Section 5, where we consider a time-periodic perturbation. The bathed system is characterized by the coarse-grained density matrix $D(t)$. Its evolution to any

order in the external perturbation is described using Floquet’s theorem. The decomposition (116) of the density matrix $D(t)$ in the operator basis provided by the operators $X_\alpha, \alpha \in \mathcal{R}$ and $Y_l, l = 1, \dots, N - 1$, which are defined in equations (86, 103, 104, 105), respectively, allows us to formulate an explicit solution. The recursion relations (119) for the coherences and the populations can be solved using simple matrix operations. The solutions for the coherences are provided by equations (126, 118). The coherences acting as source terms for the populations, the latter are found from equation (127).

The master equations (21) cover a vast variety of experimental situations, ranging from optical absorption experiments in atoms, molecules, quantum dot systems or solids, to the dynamical behavior of nuclear spins. For an adequate treatment it is of course crucial to make a physically meaningful separation of the bathed system and the bath. The separation demands a profound analysis of the considered system. From the discussion in Section 2.4 it becomes clear that the typical time scales corresponding to the bathed system and the bath system must be sufficiently different. For example, considering classical optical absorption experiments on solids, it is usually adequate to associate the bath system with the vibrational degrees of freedoms of the nuclei, the phonons. The same decomposition may be applied for the discussion of most transport experiments. For studies of the relaxation dynamics of the nuclear spins in solids by NMR experiments, it is reasonable to associate the bath with the electronic subsystem.

This work was partly supported by the Swiss National Science Foundation under Grant Nos. 2000-53832.98 and 2000-058972.99.

Appendix A: Evolution of the subsystem A under the coupling to the bath B

After integration of equation (5) and iteration we obtain

$$\begin{aligned} \rho^I(t) &= \rho^I(t_0) + \frac{i}{\hbar} \int_{t_0}^t dt' [\rho^I(t'), H_{\text{int}}^I(t')] \\ &= \rho^I(t_0) + \frac{i}{\hbar} \int_{t_0}^t dt' [\rho^I(t_0), H_{\text{int}}^I(t')] \\ &\quad + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' [[\rho^I(t_0), H_{\text{int}}^I(t'')], H_{\text{int}}^I(t')] \\ &\quad + \dots \end{aligned} \quad (\text{A.1})$$

The density matrix $\rho^I(t)$ can always be written

$$\rho^I(t) = \rho_A^I(t) \otimes \rho_B^I(t) + \eta_{AB}^I(t). \quad (\text{A.2})$$

According to our assumptions, the correlation term $\eta_{AB}^I(t)$ is generated by first- and higher-order contributions of the interaction Hamiltonian H_{int}^I . Thus, it gives rise to a second-order contribution in the first integral of the development in equation (A.1). The contributions of $\eta_{AB}^I(t)$ to

the last term containing the double integral are at least of third order and will be neglected in the following. Performing the partial-trace operation Tr_B on the expression (A.1) for $\rho^I(t)$ and keeping only contributions up to second-order, we then get for the density matrix of the subsystem A

$$\begin{aligned} \rho_A^I(t) &= \rho_A^I(t_0) + \frac{i}{\hbar} \int_{t_0}^t dt' \sum_{\alpha} [\rho_A^I(t_0), A_{\alpha}^I(t')] b_{\alpha}(t') \\ &+ \frac{i}{\hbar} \int_{t_0}^t dt' \text{Tr}_B ([\eta_{AB}^I(t_0), H_{\text{int}}^I(t')]) \\ &+ \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_{\alpha, \beta} [\rho_A^I(t_0) A_{\beta}^I(t''), A_{\alpha}^I(t')] b_{\beta\alpha}(t'', t')^* \\ &- [A_{\beta}^I(t'') \rho_A^I(t_0), A_{\alpha}^I(t')] b_{\alpha\beta}(t', t'') \\ &+ \dots \end{aligned} \quad (\text{A.3})$$

The coefficients $b_{\alpha}(t')$ and $b_{\alpha\beta}(t', t'')$ are defined by

$$b_{\alpha}(t') = \text{Tr}(\rho_B^I(t_0) B_{\alpha}^I(t')) \quad (\text{A.4})$$

and

$$b_{\alpha\beta}(t', t'') = \text{Tr}(\rho_B^I(t_0) B_{\alpha}^I(t') B_{\beta}^I(t'')). \quad (\text{A.5})$$

Exchanging the role of A and B , we obtain a similar relation for $\rho_B^I(t)$. The first-order contribution to the correlation term $\eta_{AB}^I(t)$ defined by equation (A.2) can then be determined from equation (A.3) and its analog for $\rho_B^I(t)$. We get

$$\begin{aligned} \eta_{AB}^I(t) &= \rho^I(t) - \rho_A^I(t) \otimes \rho_B^I(t) \simeq \eta_{AB}^I(t_0) \\ &+ \frac{i}{\hbar} \int_{t_0}^t dt' \left[\rho_A^I(t_0) \otimes \rho_B^I(t_0), \sum_{\alpha} (A_{\alpha}^I(t') \right. \\ &\quad \left. - a_{\alpha}(t') \mathbf{1}_A) \otimes (B_{\alpha}^I(t') - b_{\alpha}(t') \mathbf{1}_B) \right], \end{aligned}$$

where $a_{\alpha}(t')$ is the counterpart of $b_{\alpha}(t')$. Assuming $\eta_{AB}^I(t_0) = 0$ for $t_0 < t_0$, we have

$$\begin{aligned} \eta_{AB}^I(t_0) &\simeq \frac{i}{\hbar} \int_{t_0}^{t_0} dt' \left[\rho_A^I(t_0) \otimes \rho_B^I(t_0), \sum_{\alpha} (A_{\alpha}^I(t') \right. \\ &\quad \left. - a_{\alpha}(t') \mathbf{1}_A) \otimes (B_{\alpha}^I(t') - b_{\alpha}(t') \mathbf{1}_B) \right]. \end{aligned}$$

Thus, the third term on the right-hand side of the expression (A.3) for $\rho_A^I(t)$ becomes

$$\begin{aligned} &\frac{i}{\hbar} \int_{t_0}^t dt' \text{Tr}_B ([\eta_{AB}^I(t_0), H_{\text{int}}^I(t')]) = \\ &\left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \sum_{\alpha} \int_{t_0}^{t_0} dt'' \sum_{\beta} \left([\rho_A^I(t_0) A_{\beta}^I(t''), A_{\alpha}^I(t')] \right. \\ &\times (b_{\alpha\beta}(t', t'')^* - b_{\alpha}(t') b_{\beta}(t'')) \\ &- [A_{\beta}^I(t'') \rho_A^I(t_0), A_{\alpha}^I(t')] (b_{\alpha\beta}(t', t'') - b_{\alpha}(t') b_{\beta}(t'')) \\ &\left. - [\rho_A^I(t_0), A_{\alpha}^I(t')] a_{\beta}(t'') (b_{\alpha\beta}(t', t'')^* - b_{\alpha\beta}(t', t'')) \right). \end{aligned}$$

Insertion into equation (A.3) yields

$$\begin{aligned} \rho_A^I(t) &= \rho_A^I(t_0) + \frac{i}{\hbar} \int_{t_0}^t dt' \sum_{\alpha} [\rho_A^I(t_0), A_{\alpha}^I(t')] b_{\alpha}(t') \\ &+ \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \sum_{\alpha} \int_{t_0}^{t'} dt'' \sum_{\beta} \left([\rho_A^I(t_0) A_{\beta}^I(t''), A_{\alpha}^I(t')] \right. \\ &\times b_{\alpha\beta}(t', t'')^* - [A_{\beta}^I(t'') \rho_A^I(t_0), A_{\alpha}^I(t')] b_{\alpha\beta}(t', t'') \\ &- \frac{i}{\hbar} \int_{t_0}^t dt' \sum_{\alpha} [\rho_A^I(t_0), A_{\alpha}^I(t')] \\ &\times \frac{i}{\hbar} \int_{t_0}^{t_0} dt'' \sum_{\beta} (b_{\alpha\beta}(t', t'')^* - b_{\alpha\beta}(t', t'')) a_{\beta}(t'') \\ &\left. - \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \sum_{\alpha} \int_{t_0}^{t_0} dt'' \sum_{\beta} [\rho_A^I(t_0), A_{\beta}^I(t'')] \right. \\ &\quad \left. A_{\alpha}^I(t') \right] b_{\beta}(t'') b_{\alpha}(t'). \end{aligned} \quad (\text{A.6})$$

Note that the whole influence of the subsystem B on the subsystem A is carried solely by the functions $b_{\alpha}(t')$ and $b_{\alpha\beta}(t', t'')$, and that these functions depend only on the initial statistical state $\rho_B^I(t_0)$ of the subsystem B . Clearly, the roles of the subsystems A and B are interchangeable. Accordingly, a relation similar to equation (A.6) holds also for $\rho_B^I(t)$.

Let us now consider the situation where the subsystem B behaves like a bath. Its fluctuations around statistical equilibrium are generated by the dynamical coupling with the subsystem A . In the Schrödinger picture, the density matrix of the subsystem B may then be written

$$\rho_B(t) = \rho_B^0 + \delta\rho_B(t)$$

with

$$[\rho_B^0, H_B] = 0.$$

The fluctuation term $\delta\rho_B(t)$ may be associated with the first- and higher-order contributions. We introduce the mean values

$$b_{\alpha}^0 \equiv \text{Tr}(\rho_B^0 B_{\alpha})$$

to rewrite the total Hamiltonian as

$$\begin{aligned} H &= \left(H_A + \sum_{\alpha} A_{\alpha} b_{\alpha}^0 \right) \otimes \mathbf{1}_B + \mathbf{1}_A \otimes H_B \\ &\quad + \sum_{\alpha} A_{\alpha} \otimes (B_{\alpha} - b_{\alpha}^0 \mathbf{1}_B). \end{aligned}$$

This corresponds to the replacements (7). Obviously, after these replacement the mean values b_{α}^0 vanish and the coefficients $b_{\alpha}(t')$ in equation (A.6) depend at least to first order on the interaction. We see immediately that the last term in equation (A.6) vanishes, if we restrict ourselves to terms up to second order in the interaction. The second

term in equation (A.6) depends on the coefficients $b_\alpha(t')$. In order to calculate $b_\alpha(t')$ we start from the equivalent of equation (A.6) for the subsystem B evaluated to first order. We then get

$$\rho_B^I(t_0) = \rho_B^0 + \frac{i}{\hbar} \int_{t_{00}}^{t_0} dt'' \sum_{\beta} [\rho_B^I(t_0), B_\beta^I(t'')] a_\beta(t'').$$

Inserting the above expression into equation (A.4), we obtain

$$\begin{aligned} b_\alpha(t') &= \frac{i}{\hbar} \int_{t_{00}}^{t_0} dt'' \sum_{\beta} \text{Tr}([\rho_B^I(t_0), B_\beta^I(t'')] B_\alpha^I(t')) a_\beta(t'') \\ &= \frac{i}{\hbar} \sum_{\beta} \int_{t_{00}}^{t_0} dt'' (b_{\alpha\beta}(t', t'')^* - b_{\alpha\beta}(t', t'')) a_\beta(t'') \end{aligned} \quad (\text{A.7})$$

Replacing $b_\alpha(t')$ in the second term in equation (A.6) with the above expression, we find that this term and the fourth term cancel each other.

The resulting expression $\rho_A^I(t)$ depends on the functions $b_{\alpha\beta}(t', t'')$ defined in equation (A.5). Restricting ourselves to the second-order contributions to $\rho_A^I(t)$ with respect to the modified interaction term, we can replace $\rho_B^I(t_0)$ by ρ_B^0 , i.e., we approximate

$$b_{\alpha\beta}(t', t'') \simeq c_{\alpha\beta}(t' - t''),$$

where

$$\begin{aligned} c_{\alpha\beta}(t' - t'') &= c_{\beta\alpha}(t'' - t')^* \equiv \text{Tr}(\rho_B^0 B_\alpha^I(t') B_\beta^I(t'')) \\ &\equiv \text{Tr}(\rho_B^0 e^{iH_B(t' - t'')/\hbar} B_\alpha e^{-iH_B(t' - t'')/\hbar} B_\beta) \end{aligned}$$

are the correlation functions of the observables $B_\alpha^I(t')$ and $B_\beta^I(t'')$ for the subsystem B in the statistical equilibrium described by the density matrix ρ_B^0 . This proves equation (8).

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