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Nonequilibrium Aspects of Quantum Thermodynamics

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To my parents and Mirjam

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1. Introduction

Eine Theorie ist desto eindrucksvoller, je größer die Einfachheit ihrer Prämissen ist, je verschiedenartigere Dinge sie verknüpft und je weiter ihr Anwendungsbereich ist. Deshalb der tiefen Eindruck, den die klassische Thermodynamik auf mich machte. Es ist die einzige physikalische Theorie allgemeinen Inhalts, von der ich überzeugt bin, daß sie im Rahmen der Anwendbarkeit ihrer Grundbegriffe niemals umgestoßen werden wird (zur besonderen Beachtung der grundsätzlichen Skeptiker).

A. Einstein [129]

Phenomenological thermodynamics and statistical mechanics are part of the most impressive and far-reaching theories of modern physics: Their implications reach from central technical devices of the contemporary human society, like heat engines and refrigerators etc. to recent physics at almost all length scales, from Bose-Einstein-condensates and superconductors to black holes.

After a phenomenological introduction by some early scientists (Celsius, Fahrenheit, etc.) of quantities from our everyday experiences like temperature and pressure, the whole picture dramatically changed with Joule's calculation of the heat equivalent in 1840. This celebrated investigation showed that heat is nothing else but energy. Joule thus opened a connection between early thermodynamics and (by this time already advanced) classical Hamiltonian mechanics.

In 1866 Boltzmann was able to reduce thermodynamics entirely to classical mechanics by identifying the so far phenomenological entropy with the volume of a certain region in phase space [7]. Finally, this conjecture led to our modern understanding of thermodynamics. Besides Boltzmann, such famous physicists as Gibbs [43], Ehrenfest [25], Birkhoff [5] and von Neumann [110] tried to prove the celebrated postulate, but did not succeed without using some further assumptions like ergodicity, quasi-ergodicity, molecular chaos etc. which could neither be proven, in general. Nevertheless, thermodynamics

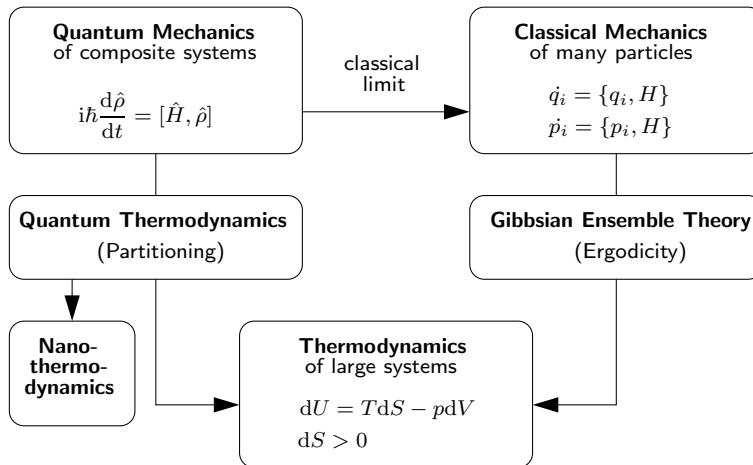


Figure 1.1.: Foundation of thermodynamics on quantum mechanics (left) or classical mechanics (right), respectively.

has proven to be an extremely effective description of many physical processes.

In those early days most people thought about a thermodynamical system, e.g. a gas, being a classical multi particle system – bouncing balls in a box. With the development of quantum mechanics at the beginning of the 20th century such a classical idea of a gas system became questionable. Of course, that does not categorically mean that everything has to be done quantum mechanically if a simpler effective description is available. Nevertheless, the foundation of thermodynamics on classical Hamiltonian mechanics faces several conceptual problems.

To overcome those deficiencies, there have been several recent approaches to thermodynamical behavior from quantum mechanics [45, 46, 116, 149]. A very successful approach by Gemmer and Mahler [36, 37, 40, 41] underlines the important role of entanglement between the considered system and the rest of the world for the emergence of thermodynamical behavior. Thus, an extremely non-classical property turns out to be responsible for the everyday experience of enforcement of the equilibrium. Fortunately this foundation comes without any further assumptions and has been called *Quantum Thermodynamics* (see [40]). Such a quantum mechanical foundation does not only clarify the background of irreversible behavior in terms of a reversible microscopic theory, but also contains the chance to extend some thermodynamical concepts to situations where the preconditions for the theory itself are (in part) violated (cf. Fig. 1.1).

Having established a theory of equilibrium quantum thermodynamics, questions about the stability of the equilibrium arise, whichever microscopic foundation of the theory one prefers. Those questions mainly address the reaction of a system weakly perturbed from the outside, i.e. moved out of its respective equilibrium state. The most important ones refer to the *relaxation to equilibrium* and the properties of *stationary local equilibrium states* [82]. The latter corresponds to a situation where the system is fixed in a *nonequilibrium* situation by conflicting constraints from the outside. These constraints may be given by very large, eventually infinite reservoirs of energy, mass, charge etc, featuring different intensive parameters, i.e. temperatures, chemical potentials etc. In contrast, a relaxation to equilibrium emerges from a coupling to such an environment as well, but there are no competing reservoirs of different intensive parameters present. Thus the system finally reaches the global equilibrium, and will not be forced to stay in a stationary local equilibrium state, featuring energy, temperature or concentration gradients as well as currents of the respective quantities.

While the existence of a final equilibrium is a major topic of equilibrium thermodynamics, the research in nonequilibrium thermodynamics is more interested in the route to this final stationary state as well as the time the system needs for its relaxation process. Furthermore, there could be some differences between the time scale of reaching the thermal equilibrium and the decay of the correlations within the system. Especially for modern quantum information processing [111], decoherence [44, 64, 160, 161] (i.e. decay of correlations) plays a crucial role.

In both situations either the relaxation or the stationary local equilibrium scenario pose central questions about the type of transport of energy, heat, mass, charge etc through the respective system. In our classical world we typically find diffusive (statistical) transport, expressed by such famous results as Fourier's Law [33] of heat conduction and Fick's Law [31] of particle transport. On the other hand some systems feature ballistic transport, i.e. the conductivity diverges [92, 114, 115, 120]. Such materials do not show any resistivity for the transport [19], and thus a current of the respective quantity flows in the system without any stimulus, e.g. electrical superconductivity. Interestingly enough, it is the normal transport that appears to be harder to explain, whichever microscopic theory is used. Thus, some researchers claim that a satisfactory derivation of e.g. Fourier's Law from truly fundamental principles was still missing [14].

Besides the growing interest in old concepts like temperature and entropy at the nanoscale, theories of relaxation and transport have recently regained a lot of attention. This renaissance follows not only from the above described fundamental reasons, but also from some practical ones: In a time where electronic

circuits and computer chips are getting smaller and smaller, the equilibrium and nonequilibrium thermodynamics (linear irreversible thermodynamics) at small length scales far below the thermodynamic limit (particle number to infinity), gain in importance [67, 119, 133, 155]. The rapid miniaturization relies on the controlled theoretical understanding of original macroscopic processes, e.g. transport of energy, heat, charge, mass, magnetization etc. Only from the foundations of a theory its limits of applicability may be inferred. Thus the ongoing technological progress and the lack of a satisfactory microscopic foundation brings one back to rather fundamental questions.

The present study is intended to address some aspects of the far-reaching topics of *relaxation* and *transport*. In “good old tradition” we will investigate those interesting fields again from first principles – standard quantum mechanics. Besides the use of the theory of open quantum systems, both these topics will be considered by the new and powerful quantum thermodynamical technique the – *Hilbert Space Average Method*. This background already contains one of the main ideas, namely that the apparently separate fields of relaxation and transport are ruled by the same fundamental principles.

This investigation is basically devided into two central parts: The first part addresses the relaxation processes in small quantum mechanical systems due its coupling to finite as well as infinite reservoirs. The second part deals with transport of heat and energy in relaxation processes as well as stationary nonequilibrium states.

Part I.

Relaxation to Equilibrium

2. System and Environment

Quantum mechanical systems must be regarded as open systems. [...] this is due to the fact that, like in classical physics, any realistic system is subjected to a coupling to an uncontrollable environment which influences it in a non-negligible way.

H.-P. Breuer and F. Petruccione in [13]

In order to investigate the thermodynamical relaxation of a quantum mechanical system from an arbitrary state at the beginning into the global “equilibrium state” we need a single important ingredient: The system has to be coupled to some environment – another large quantum system, or even a heat bath – to model a proper thermodynamical situation. Without such a partition scheme, a deviation of the “world” into a part of interest and the rest, we would not expect any thermodynamical behavior at all. This seems to be obvious by thinking of the dynamics of a small closed quantum system, e.g. the Rabi oscillations of a pair of coupled spins. However, note that this does not mean that it is impossible to build up the “whole world” by the same small subunits coupled together. At least, one has to partition such a large modular quantum system into a part (some subunits) of interest and the whole rest.

Within the system of interest a further sub-structure is not required. The system has to be characterized by its Hamiltonian, defining some energy spectrum consisting of several energy levels and eigenstates. As just mentioned, however, in physics systems are often build up of smaller identical subunits. These smaller identities are coupled to their direct neighborhood by some interaction, leading to energy transfer and the formation of correlations respectively entanglement. Besides being part of our every day experience, such topological structures will become a central prerequisite for nonequilibrium investigations like heat conduction. Obviously, for the transfer of heat from a position A to another position B the system needs to be structured in position space. Thus, we will immediately consider such modular constructed systems here.

In the following the respective model we have in mind consists of several

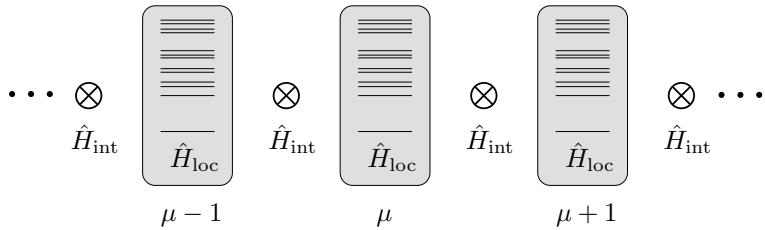


Figure 2.1.: Modular constructed model system, according to the Hamiltonian (2.1).

subunits defined by their local spectra coupled together by an interaction between adjacent subunits. Thus, the whole system forms a topological structure in real space. Additionally, this system of interest could be coupled to a single environment (investigation of its relaxation behavior) or even to several environmental systems of different properties (transport scenario). Because of the topological structure of the system itself, it could either be coupled globally to the mentioned environment or via the edges, the surface of the system, only. Let us now start with the description of the modular system and its Hamiltonian, followed by the definition of the environment.

2.1. Class of Model Systems

In quantum mechanics systems are described by a Hamilton operator \hat{H} defined in the respective Hilbert space \mathcal{H} of the system. Here, the class of systems is constructed of several subunits, n -levels each, coupled by different types of interactions (see Fig. 2.1). Therefore the Hamiltonian of the complete system consists of a local part for each subunit μ , $\hat{H}_{\text{loc}}(\mu)$, and an interaction, \hat{H}_{int} . In the following we concentrate on one-dimensional systems (chains) of N subunits and therefore only on a next neighbor interaction of adjacent subunits. Accordingly, the complete n^N -dimensional Hamiltonian reads

$$\hat{H} = \sum_{\mu=1}^N \hat{H}_{\text{loc}}(\mu) + \frac{\lambda}{\lambda_0} \sum_{\mu=1}^{N-1} \hat{H}_{\text{int}}(\mu, \mu+1), \quad (2.1)$$

where λ refers to the coupling strength of the subunits. For λ to characterize the total coupling strength it is necessary to normalize the interaction via

$$\lambda_0^2 = \frac{1}{n^{2N}} \text{Tr} \left\{ \left(\sum_{\mu=1}^{N-1} \hat{H}_{\text{int}}(\mu, \mu+1) \right)^2 \right\} \quad (2.2)$$

i.e. by the mean of the absolute value of the interaction matrix elements.

To make sense to the splitting up of the whole system into subunits, the coupling between the parts should be in some sense weak. To quantify the weak coupling condition we have to require that the mean energy contained in the interaction is much smaller than the local energy of the individual subsystem

$$\langle \lambda \hat{H}_{\text{int}} \rangle \ll \langle \hat{H}_{\text{loc}}(\mu) \rangle . \quad (2.3)$$

Furthermore, some recent investigations show that a local temperature definition on a subunit makes only sense if the respective subunits are weakly coupled [53, 55, 57]. A strong coupling destroys the local thermodynamical behavior and the idea of single identities of subsystems would be meaningless (see also [40]). Of course we could find some strong coupled systems in nature, too, but mostly the unit considered as an individual subsystem is coupled weakly to the rest of the world to make any sense of dividing nature in such a way. Thinking of the natural devision of the world into molecules, atoms or subatomic particles for different states of matter, everybody uses the subunits which are suitable for a certain coupling model. Despite the fact that a molecule consists of several atoms, it interacts as a unity with its environment and it makes definitely no sense to consider single “strongly coupled” atoms instead of considering the complete molecule.

As a simple example for the above defined model system with the Hamiltonian (2.1), we could use *spin chains*. In terms of Pauli operators the local Hamiltonian of a subunit μ with an energy splitting ΔE can be written as

$$\hat{H}_{\text{loc}}(\mu) = \frac{\Delta E}{2} \hat{\sigma}_z(\mu) . \quad (2.4)$$

The two level systems are coupled via three alternative next neighbor interactions. Firstly, a non-resonant diagonal interaction

$$\hat{H}_{\text{NR}}(\mu, \mu + 1) = C_{\text{NR}} \hat{\sigma}_z(\mu) \otimes \hat{\sigma}_z(\mu + 1) , \quad (2.5)$$

which does not account for energy transfer between the subunits. Secondly, a resonant energy transfer interaction (Förster-Coupling), which reads in terms of Pauli-operators,

$$\hat{H}_{\text{F}}(\mu, \mu + 1) = C_{\text{F}} \left(\hat{\sigma}_x(\mu) \otimes \hat{\sigma}_x(\mu + 1) + \hat{\sigma}_y(\mu) \otimes \hat{\sigma}_y(\mu + 1) \right) . \quad (2.6)$$

Here, C_{NR} and C_{F} can be used to adjust the relative strength of these two couplings. Both of these interactions together with $C_{\text{NR}} = C_{\text{F}}$, one gets

the well known Heisenberg interaction according to the Hamiltonian $\hat{H}_H = \hat{H}_{NR} + \hat{H}_F$.

Last, but not least we use a totally random next neighbor interaction

$$\hat{H}_R(\mu, \mu+1) = \sum_{i=1}^3 \sum_{j=1}^3 p_{ij} \hat{\sigma}_i(\mu) \otimes \hat{\sigma}_j(\mu+1) \quad (2.7)$$

with normal distributed random numbers p_{ij} and variance 1. Note that p_{ij} is taken to be independent of μ , since we do not allow for any disorder¹ here. The coupling should be chosen randomly, but identical between different interacting pairs of subsystems. The random interaction is supposed to model “typical interactions” without any bias.

These concrete model systems will be used for numerical investigations in the following Chapters. Otherwise, we will concentrate on the more general form of quantum chains described by (2.1).

2.2. Time-Evolution of Pure and Mixed States

According to quantum mechanics the time evolution of the state of a systems is given by the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle . \quad (2.8)$$

A formal solution of this equation in terms of the unitary time evolution operator $\hat{U}(t, t_0)$ from initial time t_0 until t is given by

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle . \quad (2.9)$$

Substituting this equation into the Schrödinger equation (2.8) we find the time-evolution equation of the operator $\hat{U}(t, t_0)$

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0) . \quad (2.10)$$

For a time independent Hamiltonian one can integrate this equation finding a formal solution for the time-evolution operator

$$\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} . \quad (2.11)$$

¹Recently, there were some interesting investigations on the influence of disorder (quantum chaos) on the thermodynamical behavior of chains of quantum systems [98, 145], but a detailed discussion would be beyond the scope of this text.

If the system is not in a pure state $|\psi\rangle$ at the beginning, but in a mixture of several pure states, we have to describe it by a density operator $\hat{\rho}$. Starting from a mixture with coefficients w_i

$$\hat{\rho}(t_0) = \sum_i w_i |\psi_i(t_0)\rangle\langle\psi_i(t_0)|, \quad (2.12)$$

using the time evolution operator of the states (2.9) to account for

$$\hat{\rho}(t) = \sum_i w_i \hat{U}(t, t_0) |\psi_i(t_0)\rangle\langle\psi_i(t_0)| \hat{U}(t, t_0)^\dagger = \hat{U}(t, t_0) \hat{\rho}(t_0) \hat{U}(t, t_0)^\dagger \quad (2.13)$$

one eventually finds by differentiating this equation (cf. [134]) the celebrated Liouville-von-Neumann equation

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}]. \quad (2.14)$$

Switching from considerations in the Hilbert space \mathcal{H} of the system to the Liouville space \mathcal{L} , the space of all operators belonging to the respective Hilbert space, it is convenient to write the last equation as

$$\frac{d}{dt} \hat{\rho}(t) = \hat{\mathcal{L}} \hat{\rho}(t), \quad (2.15)$$

defining $\hat{\mathcal{L}}$, the so-called *Liouville operator*, as a super operator² acting on operators of the Hilbert space (see [128]), here the density operator.

The respective Liouville operator above only describes a coherent time evolution of the closed quantum system. Thus, so far the Liouville-von-Neumann equation (2.15) produces the Schrödinger dynamics of a mixed state, i.e. the von Neumann entropy³ of the complete system remains constant. In the next Chapter, the Liouvillian will be extended to a more general form containing also, e.g. damping introduced by a coupling to an external environment. Thus, the environment itself will not be described as a real, i.e. microscopic quantum mechanical system, but only by its action on the system, e.g. the enforcement of an equilibrium state in the system. In order to approach such a Liouvillian, it will be necessary to consider an open quantum system instead of a closed one. This results into equilibration and the approach of a maximum entropy state in the considered system, thus, a thermodynamical situation.

²In fact a super operator is a tensor of higher order. But, transforming the density operator to a vector form it is again possible to write the Liouvillian as a tensor of second order (matrix) of squared dimension.

³Here, the von Neumann entropy only depends on the “mixedness” of the respective initial state.

The only restriction on the respective super operator $\hat{\mathcal{L}}$, whether coherent or not, is that the respective dynamics has to map a density operator again to a density operator. That means that the properties of a density operator like Hermiticity, positivity and normalizations keep conserved while the time-evolution of the system is being described by (2.15). In 1974 Lindblad [90, 91] introduced the most general form of such an Liouvillian, exactly meeting all the above properties.

Analogously to the Hilbert space, one could construct a formal solution of the Liouville-von-Neumann equation for time independent Liouville operators, too

$$\hat{\rho}(t) = e^{\hat{\mathcal{L}}(t-t_0)} \hat{\rho}(t_0), \quad (2.16)$$

defining the time-evolution operator in Liouville space [29, 32]. This, of course, could be written in case of a coherent Liouvillian (Hamiltonian dynamics only) as

$$e^{\hat{\mathcal{L}}(t-t_0)} \hat{\rho}(t_0) = e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} \hat{\rho}(t_0) e^{\frac{i}{\hbar} \hat{H}(t-t_0)}, \quad (2.17)$$

which is not the case for a decoherent Liouvillian, since such dynamics can simply not to be described by a Hamiltonian operator.

Since (2.15) is a system of differential equations and therefore $\hat{\mathcal{L}}$ simply a matrix in the higher dimensional Liouville space, we also introduce “vectors” in this space as $|\hat{\rho}\rangle$ rewriting the Liouville-von-Neumann equation

$$\frac{d}{dt} |\hat{\rho}\rangle = \hat{\mathcal{L}} |\hat{\rho}\rangle. \quad (2.18)$$

Note that not all of these vectors in Liouville space have to be also density operators, due to the respective conditions for density operators: Normalization, positive definiteness and Hermiticity. Thus, e.g. most eigenvectors of $\hat{\mathcal{L}}$ are no density operators. Furthermore, $\hat{\mathcal{L}}$ as a matrix is not necessarily hermitian and therefore the eigensystem may also not be orthogonal.

2.3. Environment or Heat Bath

So far, we have considered the time evolution of a completely isolated closed quantum system without any interaction to another system. Especially for small quantum systems, we do not expect any thermodynamical behavior in the above described time evolution. For a coupled two spin system, e.g., we get Rabi oscillations, but no decay to a stationary thermal equilibrium state.

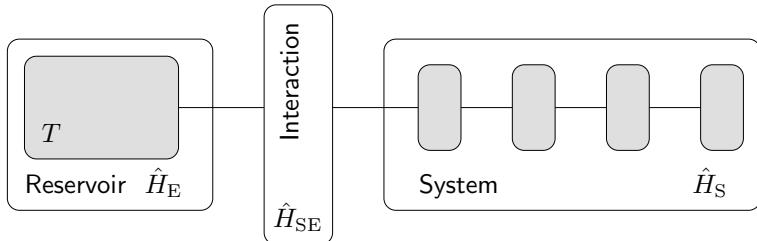


Figure 2.2.: Small system S which is of some interest to the observer coupled to a very large reservoir E with temperature T (environment) due to the Hamiltonian (2.19). Interaction between system and reservoir \hat{H}_{SE} may be local or global.

In the following we consider an open quantum system – a small system S which is of some interest to the observer coupled to a very large environment E (see Fig. 2.2). Together, system S and environment E again are a closed system in the above described sense. The state of system S does not only depend on its own unitary dynamics, but also on the interaction with the environment E, thus, it is not possible to describe the time-evolution of the system S alone by some Hamiltonian unitary dynamics. Starting from the time-evolution of the whole system according to the Hamiltonian

$$\hat{H} = \hat{H}_S \otimes \hat{1} + \hat{1} \otimes \hat{H}_E + \lambda \hat{H}_{SE} = \hat{H}_0 + \lambda_E \hat{H}_{SE}, \quad (2.19)$$

with the local Hamiltonians of system \hat{H}_S and environment \hat{H}_E and some interaction \hat{H}_{SE} (λ_E interaction strength), we are only interested in the density operator of the system S.

One may think of the environment to be a system of many uncoupled harmonic oscillators, a phonon heat bath⁴ or a spin bath consisting of an infinite amount of uncoupled or coupled spins [131]. Another important type of environment is just a multi level system with some spectral structure like introduced in quantum thermodynamics (cf. [40]). Keeping a finite number of levels we will call such a system a *finite environment*. Such a system could be a single molecule or harmonic oscillator or even a single quantum dot.

By tracing out all environmental degrees of freedom from the Liouville-von-Neumann equation (2.14) of the complete system (system and environment together) one finds for the time-evolution of the reduced density operator of the system of interest

$$\frac{d}{dt} \hat{\rho}_S(t) = -\frac{i}{\hbar} \text{Tr}_E \{ [\hat{H}, \hat{\rho}_{SE}(t)] \}. \quad (2.20)$$

⁴Spin-boson model [75, 136, 137] or Caldeira-Legett model [15, 16]

Unfortunately this equation is not a closed equation for the system S, since the right hand side depends on degrees of freedom of the environment.

Since in most cases it is not possible to consider the above described bipartite system in full detail, because the environment is by far too big, we have to use some approximation schemes to get an equation of motion for the system S exclusively. This time-dependent equation should no longer contain any variable of the environment. Only the influence of the surroundings on the system considered should enter the dynamical equation.

In the following we will describe two methods which use totally different approximation schemes. The first one will be the *Quantum Master Equation* (QME) and as a second one we will present a recently developed method, the *Hilbert Space Average Method* (HAM). Since equilibrium quantum thermodynamics predicts a thermodynamical behavior even for very small systems (see [40]) we also hope to find a *statistical relaxation* to the thermal equilibrium in not too big systems. Then we could test the validity of the approximations in comparison to the solution of the exact Schrödinger dynamics of the whole system (system and bath together).

3. Open System Approach to Relaxation Processes

From the physical point of view the simplifying assumptions¹ are unfortunately rather restrictive and it is not clear how one should remove them. There remains the basic problem in which sense the master equation approximates the Liouville equation.²

G.E. Uhlenbeck in [150]

A very common and even familiar way to consider the decay of a quantum system from a nonequilibrium initial state to the global equilibrium, due to a contact with some reservoir, is the *quantum master equation* (QME). In this Chapter we will discuss the central ideas behind this celebrated approach. The mentioned technique is inspired by the phenomenological observation that a relaxation to equilibrium is typically connected to some exponential behavior – say an exponential decay to the final global equilibrium state. A central aspect within the following discussion refers to the interaction of system S with an infinite environment E which forces the system itself to equilibrium. Finally, we end up with an equation which only contains the coherent dynamics of the system S and the action of the very large environment E on it. The equation of motion should not contain any degrees of freedom of the environmental system any longer, being therefore a *closed equation for the open system S*. We start with the time dependent Schrödinger equation of the *closed system* – system plus environment – using several approximation schemes to deduce a closed equation for the system of interest alone.

¹This essentially refers to the Markov assumption.

²In a talk on “Brownian motion” in the seminar of theoretical physics in Stuttgart J. Vollmer uses this statement to emphasize that correlations in the density *memorize* the past evolution of the system.

3.1. Nakajima-Zwanzig Equation

There are several approaches to a closed equation describing only the dynamics of the system without any concrete environment modeled. The environment only enters this equation in terms of its influence onto the system (driving the system, e.g. to equilibrium). Finally, all of these techniques could be summarized under the label *quantum master equation* (QME).

Following here Nakajima [109]³ and Zwanzig [162, 163] the reduction to the density operator of the relevant system S could be done by the super operator $\hat{\mathfrak{P}}$, a projection operator, defined by its action (see [13])

$$\hat{\mathfrak{P}}|\hat{\rho}\rangle = \text{Tr}_E \{ \hat{\rho} \} \otimes \hat{\rho}_E , \quad (3.1)$$

where $\hat{\rho}_E$ is a fixed state of the environment. The idea behind this environmental state refers to the assumption of a very large environment which does not change its state within the considered decay time of the system. Furthermore, we define a projection operator $\hat{\mathfrak{Q}}$ which projects on the irrelevant part of the density operator

$$\hat{\mathfrak{Q}}|\hat{\rho}\rangle = |\hat{\rho}\rangle - \hat{\mathfrak{P}}|\hat{\rho}\rangle . \quad (3.2)$$

The time-evolution of the density operator of the whole system in the Dirac or interaction picture reads

$$\frac{\partial}{\partial t}|\hat{\rho}(t)\rangle = -i\hbar\lambda [\hat{H}_{\text{int}}(t), \hat{\rho}(t)] = \lambda \hat{\mathfrak{L}}(t) |\hat{\rho}(t)\rangle , \quad (3.3)$$

with the definition of the time-dependent interaction Hamiltonian in the Dirac picture using the transformation (2.11)

$$\hat{H}_{\text{int}}(t) = \hat{U}^\dagger(t, 0) \hat{H}_{\text{int}} \hat{U}(t, 0) = e^{\frac{i}{\hbar} \hat{H}_0 t} \hat{H}_{\text{int}} e^{-\frac{i}{\hbar} \hat{H}_0 t} \quad (3.4)$$

as well as the appropriate super operator $\hat{\mathfrak{L}}(t)$.

Projecting out the relevant respectively irrelevant part of the Liouville-von-Neumann equation (3.3) we find two equations

$$\frac{\partial}{\partial t} \hat{\mathfrak{P}}|\hat{\rho}(t)\rangle = \lambda \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) |\hat{\rho}(t)\rangle , \quad (3.5)$$

$$\frac{\partial}{\partial t} \hat{\mathfrak{Q}}|\hat{\rho}(t)\rangle = \lambda \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(t) |\hat{\rho}(t)\rangle . \quad (3.6)$$

³Note that the approach in the cited paper is slightly different from what is done here. The projection operator used by Nakajima projects on the diagonal respectively off-diagonal part of the density operator instead of the system respectively environmental part.

According to the definition of the super operators (3.1) and (3.2) the unit operator of the complete Liouville space has the expansion $\hat{\mathbf{1}} = \hat{\mathfrak{P}} + \hat{\mathfrak{Q}}$ (cf. [13]) and therefore we rewrite

$$\frac{\partial}{\partial t} \hat{\mathfrak{P}} |\hat{\rho}(t)\rangle = \lambda \left(\hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{P}} + \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{Q}} \right) |\hat{\rho}(t)\rangle , \quad (3.7)$$

$$\frac{\partial}{\partial t} \hat{\mathfrak{Q}} |\hat{\rho}(t)\rangle = \lambda \left(\hat{\mathfrak{Q}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{P}} + \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{Q}} \right) |\hat{\rho}(t)\rangle . \quad (3.8)$$

In order to get a closed equation for the relevant subspace we have to solve the second equation first. The formal solution of the homogeneous equation

$$\frac{\partial}{\partial t} \hat{\mathfrak{Q}} |\hat{\rho}(t)\rangle = \lambda \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{Q}} |\hat{\rho}(t)\rangle , \quad (3.9)$$

taking into account that the operator on the right hand side is time-dependent, reads

$$\hat{\mathfrak{Q}} |\hat{\rho}(t)\rangle := \hat{\mathfrak{W}}(t, s) = \hat{\mathfrak{T}} \exp \left\{ \lambda \int_s^t ds' \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(s') \right\} \quad (3.10)$$

with time ordering operator $\hat{\mathfrak{T}}$. For the initial state $\hat{\mathfrak{Q}}|\hat{\rho}(t_0)\rangle$ one finds

$$|x_{\text{hom}}(t)\rangle = \hat{\mathfrak{W}}(t, t_0) \hat{\mathfrak{Q}} |\hat{\rho}(t_0)\rangle . \quad (3.11)$$

According to the Greens function technique, an ansatz for the particular solution of the inhomogeneous equation for an initial state $|\hat{\rho}(t_0)\rangle$ is

$$|x_{\text{part}}(t)\rangle = \lambda \int_{t_0}^t ds \hat{\mathfrak{W}}(t, s) \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(s) \hat{\mathfrak{P}} |\hat{\rho}(s)\rangle . \quad (3.12)$$

Finally, we find the formal solution of (3.8)

$$\begin{aligned} \hat{\mathfrak{Q}} |\hat{\rho}(t)\rangle &= |x_{\text{hom}}(t)\rangle + |x_{\text{part}}(t)\rangle \\ &= \hat{\mathfrak{W}}(t, t_0) \hat{\mathfrak{Q}} |\hat{\rho}(t_0)\rangle + \lambda \int_{t_0}^t ds \hat{\mathfrak{W}}(t, s) \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(s) \hat{\mathfrak{P}} |\hat{\rho}(s)\rangle . \end{aligned} \quad (3.13)$$

Plugging the formal solution (3.13) into (3.7) leads to the Nakajima-Zwanzig equation

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\mathfrak{P}} |\hat{\rho}\rangle &= \lambda \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{W}}(t, t_0) \hat{\mathfrak{Q}} |\hat{\rho}(t_0)\rangle + \lambda \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{P}} |\hat{\rho}(t)\rangle \\ &\quad + \lambda^2 \int_{t_0}^t ds \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{W}}(t, s) \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(s) \hat{\mathfrak{P}} |\hat{\rho}(s)\rangle . \end{aligned} \quad (3.14)$$

3.2. Born Approximation

Firstly, we consider the second term on the right hand side of (3.14). In Hilbert space notation it reads

$$\begin{aligned}
\hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{P}} |\hat{\rho}(t)\rangle &= \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \text{Tr}_E \{ \hat{\rho}(t) \} \otimes \hat{\rho}_E \\
&= \hat{\mathfrak{P}} \left(-\frac{i}{\hbar} [\hat{H}_{\text{int}}(t), \text{Tr}_E \{ \hat{\rho}(t) \} \otimes \hat{\rho}_E] \right) \\
&= -\frac{i}{\hbar} \text{Tr}_E \left\{ [\hat{H}_{\text{int}}(t), \text{Tr}_E \{ \hat{\rho}(t) \} \otimes \hat{\rho}_E] \right\} \otimes \hat{\rho}_E \\
&= -\frac{i}{\hbar} \left(\text{Tr}_E \left\{ \hat{H}_{\text{int}} \text{Tr}_E \{ \hat{\rho}(t) \} \otimes \hat{\rho}_E \right\} \right. \\
&\quad \left. - \text{Tr}_E \left\{ \text{Tr}_E \{ \hat{\rho}(t) \} \otimes \hat{\rho}_E \hat{H}_{\text{int}} \right\} \right). \tag{3.15}
\end{aligned}$$

Since the trace acts only on the environmental degrees of freedom the system state could be pulled out finding

$$\hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{P}} |\hat{\rho}(t)\rangle = -\frac{i}{\hbar} \left[\text{Tr}_E \{ \hat{H}_{\text{int}} \hat{\rho}_E \}, \text{Tr}_E \{ \hat{\rho}(t) \} \right]. \tag{3.16}$$

Obviously this term could be written as an effective Hamiltonian $\text{Tr}_E \{ \hat{H}_{\text{int}} \hat{\rho}_E \}$ for the system only and may therefore be absorbed into the respective local Hamiltonian. This is not an approximation, but a feature of the special state $\hat{\rho}_E$ from (3.1) and the interaction Hamiltonian. Thus, it is often claimed that $\hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{P}} = 0$ (see [13, 82]). Note that all the above considerations are without any assumptions, finally leading to the exact equation

$$\frac{\partial}{\partial t} \hat{\mathfrak{P}} |\hat{\rho}\rangle = \lambda \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{W}}(t, t_0) \hat{\mathfrak{Q}} |\hat{\rho}(t_0)\rangle + \int_{t_0}^t ds \hat{\mathfrak{K}}(t, s) \hat{\mathfrak{P}} |\hat{\rho}(s)\rangle \tag{3.17}$$

with the super operator

$$\hat{\mathfrak{K}}(t, s) = \lambda^2 \hat{\mathfrak{P}} \hat{\mathfrak{L}}(t) \hat{\mathfrak{W}}(t, s) \hat{\mathfrak{Q}} \hat{\mathfrak{L}}(s) \tag{3.18}$$

called memory kernel.

In the following we will use a factorizing initial state⁴ $\hat{\rho}(t_0) = \hat{\rho}_S(t_0) \otimes \hat{\rho}_E$. According to the definition of the projection operator (3.1) we find that

⁴Note that in principle it is not necessary to assume such a factorizing initial condition. However it is routinely done since the first term on the right hand side of (3.17) is very complicated to treat.

$\hat{\mathfrak{P}}|\hat{\rho}(t_0)\rangle = |\hat{\rho}(t_0)\rangle$, and thus it follows from (3.2) that $\hat{\mathfrak{Q}}|\hat{\rho}(t_0)\rangle = 0$. Therefore the Nakajima-Zwanzig equation simplifies to

$$\frac{\partial}{\partial t}\hat{\mathfrak{P}}|\hat{\rho}\rangle = \lambda^2 \int_{t_0}^t ds \hat{\mathfrak{K}}(t,s) \hat{\mathfrak{P}}|\hat{\rho}(s)\rangle . \quad (3.19)$$

By expanding the memory kernel in terms of the coupling strength, namely expanding the Greens-function to second order, we obtain

$$\hat{\mathfrak{K}}(t,s) = \lambda^2 \hat{\mathfrak{P}}\hat{\mathfrak{L}}(t)\hat{\mathfrak{Q}}\hat{\mathfrak{L}}(s) + \mathcal{O}(\lambda^3) \quad (3.20)$$

and finally get a second order integro-differential equation

$$\frac{\partial}{\partial t}\hat{\mathfrak{P}}|\hat{\rho}\rangle = \lambda^2 \int_{t_0}^t ds \hat{\mathfrak{P}}\hat{\mathfrak{L}}(t)\hat{\mathfrak{L}}(s)\hat{\mathfrak{P}}|\hat{\rho}(s)\rangle , \quad (3.21)$$

where we used $\hat{\mathfrak{P}}\hat{\mathfrak{L}}(t)\hat{\mathfrak{P}} = 0$ again.

Going back to the explicit definitions of the projection and Liouville operator we find

$$\frac{\partial}{\partial t}\hat{\rho}_S = -\frac{\lambda^2}{\hbar^2} \int_{t_0}^t ds \text{Tr}_E \left\{ [\hat{H}_{\text{int}}(t), [\hat{H}_{\text{int}}(s), \hat{\rho}_S(s) \otimes \hat{\rho}_E]] \right\} \quad (3.22)$$

the so called *Born approximation* of the Nakajima-Zwanzig equation.

3.3. Redfield, Markov and the Rotating Wave Approximation

To gain a local equation in time from (3.22) we replace the system state at time s by the state $\hat{\rho}_S(t)$ at time t , obtaining the so called Redfield equation. Assuming that the integrand of (3.22) disappears for a time much bigger than the decay of the correlation function of the environment, we can rewrite (3.22) by the transformation $s \rightarrow s - t$ and let the upper limit of the integration go to infinity. Finally one finds the *Born-Markov master equation*⁵

$$\frac{\partial}{\partial t}\hat{\rho}_S = -\frac{\lambda^2}{\hbar^2} \int_{t_0}^{\infty} ds \text{Tr}_E \left\{ [\hat{H}_{\text{int}}(t), [\hat{H}_{\text{int}}(t-s), \hat{\rho}_S(t) \otimes \hat{\rho}_E]] \right\} . \quad (3.23)$$

⁵Originally the Markov assumption addresses the fact that systems typically forget about their initial conditions. However, sometimes, it is also associated with the possibility of getting a closed equation for the density operator of the system at all (cf. Sect. 7.2 and Sect. 8.3).

For these approximations to be valid the time-scales of the dynamics of system and environment must be clearly separated. The dynamics of the system has to be very slow in comparison to the decay of correlations within the environment.

For a further simplification we consider the interaction Hamiltonian in the Schrödinger picture, given by (see [13])

$$\hat{H}_{\text{int}} = \sum_{\alpha} \hat{A}_{\alpha} \otimes \hat{B}_{\alpha} . \quad (3.24)$$

Expressing the system part of the interaction Hamiltonian in the eigensystem $\hat{H}_S|n\rangle = E_n|n\rangle$ of the local Hamiltonian of system S (supposing the spectrum of the system to be discrete) we find

$$\hat{A}_{\alpha} = \sum_{n,n'} (\hat{A}_{\alpha})_{n,n'} |n\rangle \langle n'| . \quad (3.25)$$

These operators are often called *environment operators* (see [97]). The interaction Hamiltonian in the Dirac picture then reads

$$\begin{aligned} \hat{H}_{\text{int}}(t) &= e^{\frac{i}{\hbar} \hat{H}_0 t} \sum_{\alpha} \sum_{n,n'} (\hat{A}_{\alpha})_{n,n'} |n\rangle \langle n'| \otimes \hat{B}_{\alpha} e^{-\frac{i}{\hbar} \hat{H}_0 t} \\ &= \sum_{\alpha} \sum_{n,n'} (\hat{A}_{\alpha})_{n,n'} e^{\frac{i}{\hbar} \hat{H}_{\text{ST}} t} |n\rangle \langle n'| e^{-\frac{i}{\hbar} \hat{H}_{\text{ST}} t} \otimes e^{\frac{i}{\hbar} \hat{H}_{\text{E}} t} \hat{B}_{\alpha} e^{-\frac{i}{\hbar} \hat{H}_{\text{E}} t} \\ &= \sum_{\alpha} \sum_{n,n'} e^{-i\omega t} (\hat{A}_{\alpha})_{n,n'} |n\rangle \langle n'| \otimes \hat{B}_{\alpha}(t) \end{aligned} \quad (3.26)$$

with $\omega = (E_{n'} - E_n)/\hbar$. Defining the new operators

$$\hat{A}_{\alpha}(\omega) = (\hat{A}_{\alpha})_{n,n'} |n\rangle \langle n'| \quad \text{with} \quad \omega = \omega(n, n') , \quad (3.27)$$

switching from a summation over n and n' to one over ω , we finally find the interaction Hamiltonian

$$\hat{H}_{\text{int}}(t) = \sum_{\alpha} \sum_{\omega} e^{-i\omega t} \hat{A}_{\alpha}(\omega) \otimes \hat{B}_{\alpha}(t) . \quad (3.28)$$

Plugging in this interaction Hamiltonian into the master equation (3.23), neglecting all fast rotating terms (rotating wave approximation) one gets the *quantum master equation*

$$\begin{aligned} \frac{\partial \hat{\rho}_S}{\partial t} &= -\frac{i}{\hbar} [\hat{H}_{\text{Lamb}}, \hat{\rho}_S] \\ &+ \sum_{\omega} \sum_{\alpha, \beta} \gamma_{\alpha\beta}(\omega) \left(\hat{A}_{\beta}(\omega) \hat{\rho}_S \hat{A}_{\alpha}^{\dagger}(\omega) - \frac{1}{2} [\hat{A}_{\alpha}^{\dagger}(\omega) \hat{A}_{\beta}(\omega), \hat{\rho}_S]_+ \right) , \end{aligned} \quad (3.29)$$

with the transition rates given by

$$\gamma_{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} ds e^{i\omega s} \text{Tr}_E \{ \hat{B}_\alpha^\dagger(s) \hat{B}_\beta(0) \hat{\rho}_E \}, \quad (3.30)$$

the environment correlation functions. These transition rates may depend on details of the environmental system, e.g. its state density. Furthermore, both the temperature as well as the coupling strength of the environment to the system play a crucial role in the concrete value of $\gamma_{\alpha\beta}(\omega)$. As mostly done for simplicity reasons we also neglect the Lamb shift Hamiltonian \hat{H}_{Lamb} in the following.

By a diagonalization of the positive coefficient matrix $\gamma_{\alpha\beta}(\omega)$, introducing new operators \hat{L}_α called Lindblad environmental operators (see [97]), one gets the Lindblad form of the above master equation

$$\frac{\partial \hat{\rho}_S}{\partial t} = \sum_\alpha \gamma_\alpha \left(\hat{L}_\alpha \hat{\rho}_S \hat{L}_\alpha^\dagger - \frac{1}{2} [\hat{L}_\alpha^\dagger \hat{L}_\alpha, \hat{\rho}_S]_+ \right) = \hat{\mathcal{L}}_E \hat{\rho}_S, \quad (3.31)$$

with γ_α denoting the eigenvalues of $\gamma_{\alpha\beta}(\omega)$. The Lindblad form of the quantum master equation is the most general form of a closed Markovian master equation for the dynamical behavior of a system coupled to an environment. It was shown by Lindblad [90] that under the application of any *Dissipator* respectively Linblad super operator $\hat{\mathcal{L}}_E$ according to (3.31), $\hat{\rho}_S$ remains a density operator of the system with all its properties – positivity, Hermiticity and $\text{Tr} \{ \hat{\rho}_S \} = 1$.

3.4. The Dissipator

Having derived the most general form of a closed equation for the system weakly coupled to a large environment we can now present the resulting Liouville-von-Neumann equation for the open system. Therefore we have to transform (3.31) back to the Schrödinger picture, simply getting an additional coherent term according to the Hamiltonian \hat{H}_S of the system, respectively Liouvillian $\hat{\mathcal{L}}_S$, introduced in Sect. 2.1. Thus, the Liouville-von-Neumann equation for the open quantum system reads

$$\frac{\partial}{\partial t} |\hat{\rho}\rangle = (\hat{\mathcal{L}}_S + \hat{\mathcal{L}}_E(T, \lambda_E)) |\hat{\rho}\rangle. \quad (3.32)$$

(Remember, the system $\hat{\mathcal{L}}_S$ (\hat{H}_S) could be a chain of N identical subunits with n levels each, coupled weakly by a next neighbor interaction, thus living

in a Liouville space of dimension n^{2N} .) The second Liouville super operator $\hat{\mathcal{L}}_E$ refers to the action of the environment onto the system, defined by such damping operators as derived in the last Section (Markovian quantum master equation) called dissipator. The environment has to be weakly coupled to the system to make any sense to the expansion of the memory kernel in (3.20), with coupling strength λ_E . By choosing a temperature T for the environmental system we get certain absolute values for the damping rates γ_α in the respective dissipator (3.31).

Rather than writing down a concrete environmental system, and try to account for the rates and operators from the above formulas, we choose the environmental operators and the rates as phenomenological models. Mostly, the environmental operators are chosen to be raising and lowering operators of the considered system. In case the system only consists of a single two-level system ($n = 2$) we could take $\hat{\sigma}_+$ and $\hat{\sigma}_-$ as the respective Lindblad operators. Defining two damping channels with rates W_{01} and W_{10} to obtain a finite temperature one gets the super operator

$$\begin{aligned}\hat{\mathcal{L}}_E(T, \lambda_E)\hat{\rho} = & W_{10}(T, \lambda_E)(2\hat{\sigma}_-\hat{\rho}\hat{\sigma}_+ - \hat{\rho}\hat{\sigma}_+\hat{\sigma}_- - \hat{\sigma}_+\hat{\sigma}_-\hat{\rho}) \\ & + W_{01}(T, \lambda_E)(2\hat{\sigma}_+\hat{\rho}\hat{\sigma}_- - \hat{\rho}\hat{\sigma}_-\hat{\sigma}_+ - \hat{\sigma}_-\hat{\sigma}_+\hat{\rho}).\end{aligned}\quad (3.33)$$

The rates depend on the bath temperature and the coupling strength. These are standard Lindblad operators, well-known from the theory of open systems in quantum optics, which introduce the damping of the environment into the Liouville-von-Neumann equation of a two-level system. The presented operators can easily be generalized to finite $n > 2$.

For many nonequilibrium scenarios we need in the following a local coupling to the environment, i.e. via the edges of the system only. This is easily done by choosing environmental operators of the above described form, namely raising and lowering operators of the subunit at the edge times the unit operator of the rest of the system. This procedure is often criticized⁶, but for weakly coupled subunits it is a valid method, nevertheless. Since the weak coupling limit of the subunits is already necessary for a proper definition of separated subunits, as argued in Sect. 2.1, the respective assumption is not a too strong restriction regarding the model system.

A slightly different approach has been used in the literature (cf. [121, 122, 125]) by diagonalizing the system first, transforming the environment operators into this eigenbasis. (However, one has to proceed with care in case of a local environment coupling at the edge of a system, since the standard

⁶“Suppose that two systems A and A' are in contact with a heat bath B ... If the interaction ... [between A and A'] is not weak, however, the equilibrium of the composite system is not guaranteed ...” (Kubo [82, p.89])

dissipator would no longer act locally in the eigenspace of the whole system. This could eventually lead to apparently strange effects⁷, like currents flowing only at the edges, not inside the system.) Following this method one finds the dissipator in the Liouville-von-Neumann equation to be

$$\hat{\mathcal{L}}_E(T, \lambda_E)\hat{\rho} = [\hat{L}, \hat{R}\hat{\rho}] + \left([\hat{L}, \hat{R}\hat{\rho}]\right)^\dagger \quad (3.34)$$

with the Lindblad operators \hat{L} as above, and the operators \hat{R} in diagonal representation of the system Hamiltonian $\hat{H}_S|n\rangle = E_n|n\rangle$

$$\langle n|\hat{R}|n'\rangle = \frac{(E_n - E_{n'})}{e^{(E_n - E_{n'})/T} - 1} \langle n|\hat{L}|n'\rangle, \quad n \neq n' \quad (3.35)$$

and $\langle n|\hat{R}|n\rangle = 0$. There are some doubts about the plausibility of this approach, too, since the weak coupling of several identical subunits typically produces a spectrum of the complete system consisting of several bands of densely lying levels (quasi degenerate levels). Therefore we get very slowly oscillating terms and can no longer guarantee that the relaxation dynamics is much slower than the dynamics of these oscillating terms of the system⁸.

Summarizing these considerations we think that the two approaches are to some extent equivalent at least for weakly coupled systems. Furthermore, in case of weak coupling the product basis (often the natural basis for such modular systems) is a very good approximation to the real eigenbasis of the system, which supports the equivalence, too. In Chap. 4 we will present a comparison between these approximation schemes and an exact solution of the Schrödinger equation. This may show the validity of the above considerations for a set of system parameters.

⁷Eulenhofer Seminar, Stuttgart 2006, unpublished.

⁸“The corresponding condition is that the inverse frequency differences involved in the problem are small compared to the relaxation time of the system,...” (Breuer [13, p.137])

4. Global and Local Properties

The second law is arguably one of the most fundamental and far-reaching laws of physics; nevertheless, its origin remains puzzling.

J. Gemmer, A. Otte, G. Mahler in [41]

So far we have introduced a model system, which is eventually constructed of several identical subunits coupled together forming some topological structure in real space. In the last Chapter, we discussed a method to describe the coupling of such quantum systems to an environment, e.g. a heat reservoir, the quantum master equation. Finally, we have been able to derive a closed equation of motion for the open quantum system containing some incoherent damping terms describing the action of the reservoir. Thus, the respective equation of motion does not explicitly contain dynamical variables of the environment any longer.

In the present Chapter, we will investigate both global as well as local properties of the appropriate stationary state within the system of interest. However, at the moment we are not interested in so called *local equilibrium states* (see Part II), containing temperature gradients and heat currents, but in the final *global equilibrium* and the route to this stationary state. Thus, we will consider model systems coupled to a single heat bath here. In this context interesting quantities are global and local temperatures (energies) in both unstructured and structured systems.

4.1. Global Stationary Equilibrium State

Having in mind a system S coupled to an infinite environment E we describe the situation by an open system master equation for the system S containing some incoherent damping terms, i.e. a dissipator in Lindblad form. The system itself is an arbitrary multilevel system eventually constructed of several identical coupled subunits. The dissipator, a super operator according to (3.33) or (3.34), drives the model system to a stationary state, irrespective of

the initial state. In case of a thermal reservoir, this final state should be a *thermal equilibrium state*, i.e. a Gibbs state of the system S, to model a proper thermodynamical situation. The temperature of this equilibrium state is given by the temperature of the bath system, introduced by the damping rates of the dissipator. Let us show in the following that the mentioned stationary state of the open system is indeed a Gibbs state.

Starting from the Liouville-von-Neumann equation (3.32), i.e. a system S coupled to an environment E (coupling strength λ_E) with inverse temperature $\beta_E = 1/k_B T$

$$\frac{\partial}{\partial t} |\hat{\rho}\rangle = (\hat{\mathcal{L}}_S + \hat{\mathcal{L}}_E(\beta_E, \lambda_E)) |\hat{\rho}\rangle, \quad (4.1)$$

we expect the system to relax to the canonical equilibrium state, independently of the initial state. The dissipator (3.29) reads

$$\hat{\mathcal{L}}_E |\hat{\rho}\rangle = \sum_{\omega} \sum_{\alpha, \beta} \gamma_{\alpha\beta}(\omega, \beta_E, \lambda_E) \left(\hat{A}_{\beta}(\omega) \hat{\rho} \hat{A}_{\alpha}^{\dagger}(\omega) - \frac{1}{2} [\hat{A}_{\alpha}^{\dagger}(\omega) \hat{A}_{\beta}(\omega), \hat{\rho}]_{+} \right), \quad (4.2)$$

where only the rates depend on the temperature and the coupling strength of the environment. The canonical equilibrium state (Gibbs state) of the system yields

$$\hat{\rho}_{\text{eq}} = \frac{\exp(-\beta_E \hat{H}_S)}{Z} \quad (4.3)$$

with the canonical partition function $Z = \text{Tr}\{\exp(-\beta_E \hat{H}_S)\}$. Plugging (4.3) into (4.1) leads to

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} \left[\hat{H}_S, \frac{\exp(-\beta_E \hat{H}_S)}{Z} \right] + \hat{\mathcal{L}}_E(\beta_E, \lambda_E) \frac{\exp(-\beta_E \hat{H}_S)}{Z}. \quad (4.4)$$

Obviously, the first term on the right hand side has to vanish. Thus, we will concentrate on the second term in the following. According to the definition of the environment operators (3.27) and the eigenstates $|n\rangle$ of \hat{H}_S we find

$$\begin{aligned} e^{-\beta_E \hat{H}_S} \hat{A}_{\alpha}(\omega) e^{\beta_E \hat{H}_S} &= e^{-\beta_E \hat{H}_S} (\hat{A}_{\alpha})_{n.n'} |n\rangle \langle n'| e^{\beta_E \hat{H}_S} \\ &= e^{\omega \beta_E} \hat{A}_{\alpha}(\omega). \end{aligned} \quad (4.5)$$

By multiplying with $\hat{\rho}_{\text{eq}}$ from the right hand side it follows immediately

$$\hat{\rho}_{\text{eq}} \hat{A}_{\alpha}(\omega) = e^{\omega \beta_E} \hat{A}_{\alpha}(\omega) \hat{\rho}_{\text{eq}} \quad (4.6)$$

and analogously

$$\hat{\rho}_{\text{eq}} \hat{A}_\alpha^\dagger(\omega) = e^{-\omega\beta_E} \hat{A}_\alpha^\dagger(\omega) \hat{\rho}_{\text{eq}} . \quad (4.7)$$

Using these relations to commute the environment operators and the equilibrium state in the dissipator (4.2) we find

$$\begin{aligned} & \hat{\mathcal{L}}_E(\beta_E, \lambda_E) |\hat{\rho}_{\text{eq}}\rangle \\ &= \sum_{\omega} \sum_{\alpha, \beta} \gamma_{\alpha\beta}(\omega) \left(e^{-\omega\beta} \hat{A}_\beta(\omega) \hat{A}_\alpha^\dagger(\omega) \hat{\rho}_{\text{eq}} - \hat{A}_\alpha^\dagger(\omega) \hat{A}_\beta(\omega) \hat{\rho}_{\text{eq}} \right) . \end{aligned} \quad (4.8)$$

From the definition of the operators $\hat{A}_\alpha(\omega)$ in (3.27), one gets $\hat{A}_\alpha^\dagger(\omega) = \hat{A}_\alpha(-\omega)$. Furthermore it is possible to show that $\gamma_{\alpha\beta}(-\omega) = e^{-\omega\beta_E} \gamma_{\alpha\beta}(\omega)$ (see [13]). By exchanging the indices α and β in the first sum and applying the above definitions, one finds that the two terms cancel each other, observing that ω is a sum over all positive and negative frequencies. Therefore we find

$$\frac{\partial \hat{\rho}_{\text{eq}}}{\partial t} = 0 \quad (4.9)$$

and thus the canonical state or Gibbs state (with temperature β_E) is indeed a stationary equilibrium state of the Liouville-von-Neumann equation.

We also get another important insight from the above considerations: according to (4.9) we can state that

$$\frac{\partial \hat{\rho}_{\text{eq}}}{\partial t} = (\hat{\mathcal{L}}_S + \hat{\mathcal{L}}_E(\beta_E, \lambda_E)) |\hat{\rho}_{\text{eq}}\rangle = 0 . \quad (4.10)$$

This eigenequation of the Liouvillian refers to eigenvalue zero with the stationary equilibrium state being the respective eigenstate. In the following we will use this result for a numerical computation of the stationary state without solving the full time dependent problem.

4.2. Approach of Equilibrium

According to the last Section the approach of a final stationary *thermal* equilibrium state with the same temperature as the bath is obligatory for the type of Lindblad quantum master equations, irrespective of the concrete multilevel system S .

In case of a two level system or spin (see Fig. 4.1) defined by the Hamiltonian

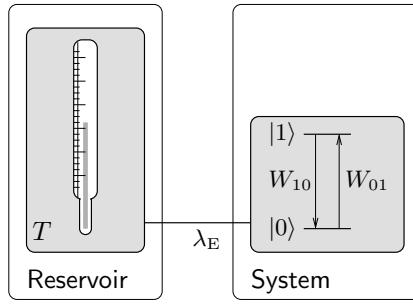


Figure 4.1.: Two level system coupled to a reservoir of temperature T .

$$\hat{H}_S = \frac{\Delta E}{2} \hat{\sigma}_z, \quad (4.11)$$

the respective stationary equilibrium state is, furthermore, reached by an exponential decay. From (3.33)¹ we get the incoherent damping part of the master equation in Lindblad form. The diagonal elements in matrix notation are given by

$$\frac{d\rho_{00}}{dt} = W_{01}\rho_{11} - W_{10}\rho_{00}, \quad (4.12)$$

$$\frac{d\rho_{11}}{dt} = W_{10}\rho_{00} - W_{01}\rho_{11}, \quad (4.13)$$

with the rates W defining the properties of the damping channels. The off-diagonal element follows

$$\frac{d\rho_{01}}{dt} = -\frac{1}{2}(W_{01} + W_{10})\rho_{01}, \quad (4.14)$$

analogously for ρ_{10} . According to an initial state $\rho_{00} = \xi$, $\rho_{11} = 1 - \xi$ one gets the exponentially decaying solution

$$\rho_{00}(t) = \frac{W_{01}}{W_{01} + W_{10}} + \left(\xi - \frac{W_{01}}{W_{01} + W_{10}}\right)e^{-(W_{01}+W_{10})t} \quad (4.15)$$

$$\rho_{11}(t) = \frac{W_{10}}{W_{01} + W_{10}} - \left(\xi - \frac{W_{01}}{W_{01} + W_{10}}\right)e^{-(W_{01}+W_{10})t}, \quad (4.16)$$

and in general for the off-diagonal element

$$\rho_{01}(t) = \rho_{01}(0)e^{-\frac{1}{2}(W_{01}+W_{10})t}. \quad (4.17)$$

¹Note that the second dissipator (3.34) leads to the same master equation in this trivial case, too.

Thus, the final global equilibrium state is exponentially reached in the limit $t \rightarrow \infty$ finding

$$\hat{\rho} = \frac{1}{W_{01} + W_{10}} \begin{pmatrix} W_{01} & 0 \\ 0 & W_{10} \end{pmatrix}. \quad (4.18)$$

In the last Section we gain the insight that this equilibrium state should be the Gibbs state cf. (4.3), i.e. we find for an energy splitting ΔE in the system a Boltzmann distribution of the diagonal elements of the density operator

$$\frac{W_{01}}{W_{10}} = e^{-\beta_E \Delta E}. \quad (4.19)$$

Furthermore, defining the coupling strength as $\lambda_E = W_{01} + W_{10}$ one gets explicit expressions for the rates in terms of the environmental coupling strength and the temperature of the reservoir

$$W_{10} = \lambda_E \frac{1}{1 + e^{-\beta_E \Delta E}}, \quad (4.20)$$

$$W_{01} = \lambda_E \frac{1}{1 + e^{\beta_E \Delta E}}. \quad (4.21)$$

Thus, the absolute value of the rates is controlled by the environmental coupling strength and the temperature of the reservoir.

4.3. Temperature

Within Quantum Thermodynamics, temperature is defined as usual by

$$\beta \equiv \frac{\partial S}{\partial E}, \quad (4.22)$$

where E refers to the internal energy of the system (see [40, 53]). Of course, here we are using the standard von-Neumann entropy S to find for a diagonal density operator

$$\hat{\rho} = \begin{pmatrix} \rho_{00} & 0 \\ 0 & \rho_{11} \end{pmatrix} \quad (4.23)$$

the entropy

$$S = -\text{Tr}\{\hat{\rho} \ln \hat{\rho}\} = -(\rho_{00} \ln \rho_{00} + \rho_{11} \ln \rho_{11}). \quad (4.24)$$

The internal energy is given by the expectation value of energy and here with (4.11) and (4.23)

$$E \equiv \text{Tr}\{\hat{\rho}\hat{H}_S\} = -\frac{\Delta E}{2}(\rho_{00} - \rho_{11}) . \quad (4.25)$$

Together with the normalization condition of the density operator $\rho_{00} + \rho_{11} = 1$ we get

$$\rho_{00} = \frac{1}{2} - \frac{E}{\Delta E}, \quad \rho_{11} = \frac{1}{2} + \frac{E}{\Delta E} . \quad (4.26)$$

Plugging this transformation into the entropy (4.24) yields

$$S(E) = - \left(\left(\frac{1}{2} - \frac{E}{\Delta E} \right) \ln \left(\frac{1}{2} - \frac{E}{\Delta E} \right) + \left(\frac{1}{2} + \frac{E}{\Delta E} \right) \ln \left(\frac{1}{2} + \frac{E}{\Delta E} \right) \right) . \quad (4.27)$$

Finally, using the definition of the inverse temperature² (4.22) we get

$$\begin{aligned} \beta &= \frac{\partial S(E)}{\partial E} = \frac{1}{\Delta E} \left(\ln \left(\frac{1}{2} - \frac{E}{\Delta E} \right) - \ln \left(\frac{1}{2} + \frac{E}{\Delta E} \right) \right) \\ &= \frac{1}{\Delta E} (\ln \rho_{00} - \ln \rho_{11}) \\ &= \frac{1}{\Delta E} \ln \frac{\rho_{00}}{\rho_{11}} . \end{aligned} \quad (4.28)$$

This is exactly what one would have gotten by directly using the Boltzmann distribution (4.19). Such a temperature definition also works for higher dimensional systems in a thermal state, i.e. a Boltzmann distribution of diagonal elements and zero off-diagonal elements in the density operator.

However, in case of only a two level system we will use the energy as a measure for temperature instead of (4.28), due to the fact that a Boltzmann distribution is always feasible here. Thus, the whole temperature scale directly maps to the energy interval $0 < T < \Delta E/2$. Of course there are also states of higher energy, e.g. the system is with 90% excited. But, those states refer to *negative temperatures* because of their inverted probabilities. In standard thermodynamical situations we may completely neglect such negative temperature states.

²Note that the inverse temperature here is a quantity with unit one over energy according to the used definition $1/\beta = k_B T$. Or one may simply use $k_B = 1$.

4.4. Local Energy and Temperature

Until now we have considered the system of interest as a whole, looking for global properties of its equilibrium state. However, the system itself could be constructed of several subunits coupled together, defining a *topological structure* in real space. For the whole system being at the respective bath temperature $\beta = \beta_E$ the question arises under what conditions also each subunit μ is in a canonical equilibrium state with the same temperature as the whole system and thus at the temperature of the reservoir $\beta(\mu) = \beta_E$. For this local temperature concept to be valid, we have to require at least a weak interaction between the subunits in comparison with the local energy splitting (remember the discussion in Sect. 2.1). However, a full investigation of this question and the conditions and circumstances for the existence of a proper local temperature is definitely beyond the scope of this text. The interested reader can find more on this topic in Refs. [53–58].

An important observable in quantum mechanics is the Hamiltonian of the system referring to the energy. Since we have decided to investigate a system consisting of several subunits with a local Hamiltonian each, coupled *weakly*³ by a next neighbor interaction (see Sect. 2.1), we will neglect the interaction energy completely, concentrating on the local energy only. For a system described by the Hamiltonian (2.1) the local energy of a subunit μ in the weak coupling limit reads

$$E(\mu) = \text{Tr}\{\hat{H}_{\text{loc}}(\mu)\hat{\rho}\}, \quad (4.29)$$

with $\hat{\rho}$ being the momentary density operator of the system. Additionally, in order to investigate energy gradients (energy differences between adjacent subunits) within the presented systems, we define the operator

$$\Delta\hat{H}_{\text{loc}}(\mu, \mu + 1) := \hat{H}_{\text{loc}}(\mu) - \hat{H}_{\text{loc}}(\mu + 1). \quad (4.30)$$

To gain the complete local information of a subunit μ it suffices to consider the reduced density operator of the respective part of the whole system

$$\hat{\rho}(\mu) = \text{Tr}_{1, \dots, \mu-1, \mu+1, \dots, N}\{\hat{\rho}\}, \quad (4.31)$$

by tracing out all other subunits. The diagonal elements of this reduced density operator of the subunit μ refer to the probabilities of being in the respective eigenstate of the local Hamiltonian \hat{H}_{loc} , whereas the off-diagonal

³Finally, Hartmann et al. [53–58] found that it mainly depends on the coupling strength of adjacent subunits, if a local temperature is properly defined. Thus, for weak couplings the definition of a local temperature is feasible.

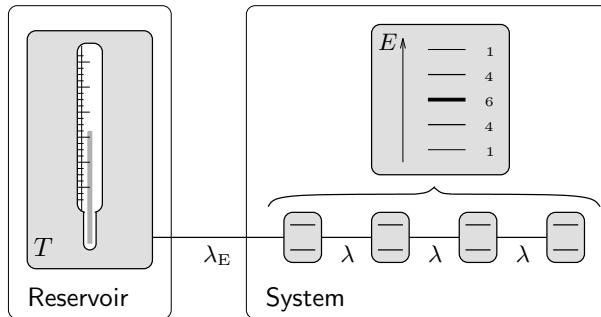


Figure 4.2.: Weakly coupled (λ) chain of spins coupled (λ_E) at the edge to a heat reservoir. Complete spectrum of diagonalized weakly coupled spin chain (inset).

elements describe correlations between these states. For a state to be thermal one has to call for vanishing off-diagonal elements and a Boltzmann distribution on the diagonal elements. Thus, the respective canonical equilibrium state reads

$$\hat{\rho}_{\text{eq}}(\mu) = \frac{\exp(-\beta \hat{H}_{\text{loc}}(\mu))}{Z(\mu)}. \quad (4.32)$$

In case of a vanishing off-diagonal part, the above given definition of a local canonical state could be used to account for the temperature of a subunit. In a numerical simulation this is simply reached by fitting the diagonal elements of the stationary local equilibrium density matrix to a Boltzmann distribution.

4.5. Open System Equilibrium State

In the previous Sections all systems were globally coupled to their environment, i.e. the Lindblad operators are defined on the complete system Hilbert space. As shown in Sect. 4.1 this has directly led to a global thermal equilibrium state and a global temperature. However, a topologically structured modular system could also be coupled only locally at a special subunit to a reservoir. Of course, such a local coupling only makes sense if the subunits are weakly coupled. This means that the subunits represent proper individuals as discussed in Sect. 2.1. For such a local coupling scenario some new questions arise: Does the system as a whole approach, nevertheless, a global thermal equilibrium state and, furthermore, what state will we find locally?

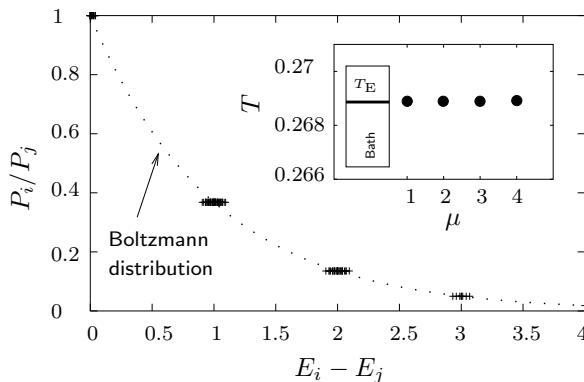


Figure 4.3.: Properties of the stationary equilibrium state of the Liouville-von Neumann equation with dissipator (3.33). For the global probability distribution in the whole system we nearly find a Boltzmann distribution. Local temperatures are exactly at the temperature of the reservoir (inset).

In the following we will consider a spin chain ($N = 4$ spins, $n = 2$) with the special Hamiltonian given in Sect. 2.1. The model system is depicted in Fig. 4.2 and consists of identical spin systems with a local level splitting of $\Delta E = 1$ and a next neighbor Heisenberg interaction (interaction Hamiltonian referring to (2.5) and (2.6) with $C_F = C_{\text{NR}} = 1$, coupling strength of $\lambda = 0.1$).

Instead of a global coupling, the system is now coupled to the heat bath via the first subunit only. Therefore we use the respective quantum master equation as derived in Chap. 3. The temperature of the reservoir is $T = 1$ which refers, in case of a single two level system, to the probability 0.2689 of being in the excited state ($\hbar = k_B = 1$). We have tuned the reservoir coupling strength to $\lambda_E = 0.01$. To show the difference between the two dissipators defined in Sect. 3.4 we have chosen a rather strong internal coupling λ compared to the external one λ_E .

Since we are mainly interested in the final stationary state of the system, we use the mentioned property of the stationary state, being an eigenstate of the Liouville operator with eigenvalue zero, to account for its density operator. The result for the dissipator (3.33) is shown in Fig. 4.3, whereas the properties of the stationary state in case of (3.34) are shown in Fig. 4.4.

In both Figures we show the ratio of two probabilities P_i finding a certain level with energy E_i populated over the energy difference of the respective levels. This should approach a Boltzmann distribution for a canonical state according to the reservoir temperature (dotted line). The crosses refer to the

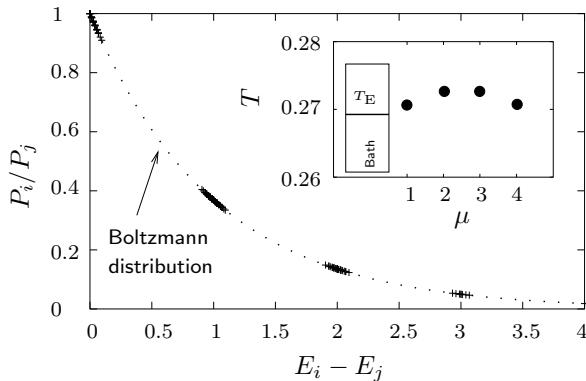


Figure 4.4.: Properties of the stationary equilibrium state of the Liouville-von Neumann equation with dissipator (3.34). For the global probability distribution in the whole system we exactly find a Boltzmann distribution. Local temperatures are approximately at the temperature of the reservoir (inset).

actual stationary equilibrium state. Inside the bands of densely lying levels only dissipator (3.34) (cf. Fig. 4.4) leads to the correct distribution. The other dissipator (3.33) (cf. Fig. 4.3) leads to an equal distribution within the bands. However, within the limit of coupling strength going to zero, where the product basis is the eigenbasis of the system, the two dissipators are equivalent.

The small insets of both Figures show the respective local temperatures of site μ using the local energy of the two level systems as a measure of temperature. For the dissipator (3.34) there are some deviations in the local temperatures compared to the global one due to the strong coupling. For a weaker coupling one can imagine that the two results will get closer to each other. The property of equal local temperatures as shown in Fig. 4.3 is a special feature of the Heisenberg chain in combination with dissipator (3.33) and gets lost for random coupling models (cf. (2.7)). Thus, inspite of the local reservoir coupling, we find a global thermal equilibrium state in the system. Furthermore, for weakly coupled subunits each single subunit is at the temperature of the reservoir.

4.6. Relaxation Dynamics in QME

Until now we have only considered the final equilibrium state reached in the limit of time going to infinity. However, in order to investigate nonequilib-

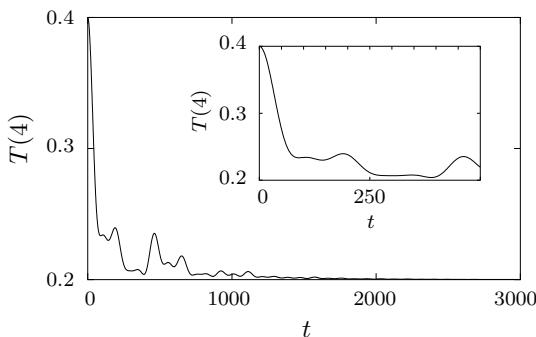


Figure 4.5.: Decay of the forth spin in a chain coupled at spin one to a bath system.
Inset: zoom of the initial behavior.

rium situations it will be necessary to observe from the beginning of the time evolution – the relaxation process to equilibrium.

Let us study the decay of a local excitation at the right hand side of the chain far away from the environment (see Fig. 4.2). We choose the initial state of the system to be a product state of a thermal equilibrium state with the bath temperature $T(\nu) = 0.2$ at each spin, but a temperature of $T(4) = 0.4$ at the last one in the chain. The heat bath is at temperature $T = 0.2$ (all temperatures are measured again in units of the local energy as argued above). Obviously, the decay of this special initial state to equilibrium in a quantum master equation model (see Fig. 4.5) is far more complicated than a simple exponential relaxation as often claimed in statistical physics.

Thus, we state here that there are several levels of statistical behavior: There is a class of systems finally reaching a global stationary equilibrium state, maybe a thermal state. Furthermore, a subclass of those models (modular systems) could additionally end with defined local temperature on each subunit. However, that does not mean that this global, respectively, global and local equilibrium is necessarily reached in a statistical manner, i.e. by an exponential decay. Obviously, a local exponential decay is only feasible in case of a diffusive transport of energy respectively heat through the chainlike system. If there is no diffusive behavior within the chain at all, the decay could be drastically different. Thus, the question about a local statistical behavior could only be answered by a consideration of transport properties of such systems, as it will be done in Part II of this text.

Let us again emphasize that there is a big difference between the thermodynamical behavior of such systems in terms of reaching a thermal equilibrium at all and the route to this state. For a more detailed analysis of local and global

properties in Quantum Thermodynamics from the point of view of a complete Schrödinger analysis and within an open system approach see [65, 66]. For the transport properties of energy through spin chains see [151].

5. Quantum Thermodynamic Environment

The use of statistical methods, essentially ignoring the dynamics, is a very powerful tool; but like a very powerful drug, it must be used with proper safeguards and under adult supervision.

H. Grad in [47]

So far and especially in the last Chapter we used the Lindblad form of the quantum master equation to write down a dynamical equation of a small system coupled to a heat reservoir. The respective master equation itself does not explicitly depend on any dynamical variable of the reservoir any longer. Just by choosing the concrete Lindblad operators (defining damping channels in the system) and the associated rates, i.e. reservoir temperatures and coupling strengths, we got an equation leading to a decay to equilibrium as well as some other properties discussed in the last Chapter.

At the beginning of this text we started with the picture of the “world” as a single very large quantum system (cf. Chap. 2). This may be constructed of a large amount of subunits coupled by some interaction. Only by structuring the whole system into a small part of interest and the rest we have approached a proper thermodynamical situation (cf. [40]). This is in contrast to the procedure of the last Chapter, where we worked on all questions concerning the system of interest without having a concrete microscopic model for the environment in mind.

Of course taking a concrete microscopic model for the environment into account, one could also use a master equation approach, e.g. starting from the Caldeira-Leggett model [15, 16] or the spin-boson model [74, 136, 137]. An accurate way would be to follow the whole derivation of the master equation step by step, checking the validity of each approximation separately. That means, e.g. to account for the respective damping rates by concretely integrating the environmental correlation functions. However, quite often the Lindblad master equation is applied without asking further questions about the envi-

ronment. Such a procedure is not necessarily inadequate. But, changing the type of the environment afterwards may lead to confusion. Thus, finally the respective dynamical equation does possibly not describe the whole system we have in mind, but something else.

Especially, after it has been shown that most of the equilibrium thermodynamical behavior can already be found in surprisingly small quantum systems (see [10, 40]), some further questions arise about the structure of the environment. One may ask, what kind of microscopic model in terms of a concrete coupling model for the environment, leads to a proper statistical, nonequilibrium behavior? Possibly such a statistical decay behavior already results by a coupling to a medium sized environment of some hundred levels only. In the following we will call such medium sized environments just *finite environment*. Since there are some fundamental prerequisites for the environmental system, e.g. its infiniteness, in open system approaches, we should not directly use a Lindblad master equation to avoid confusion. Summarizing it seems questionable whether the complicated approximation scheme – Born, Redfield, Markov, and RWA approximation – to derive the quantum master equation is at all justified for those finite environments here.

5.1. Finite Environment

In contrast to a standard infinite environment, e.g. an infinite number of harmonic oscillators, a finite environment could be a modular system of a finite amount of subunits or even a single molecule or quantum dot (cf. [39]). That also includes situations where the state of the environment is not constant within the decay time of the system. Furthermore, the environment itself does not necessarily need to be in a thermal state. Nevertheless, as we will see in the following Chapters, a statistical relaxation behavior can be induced by a coupling of such a finite environment to a small quantum system. Thus, the principles of statistical mechanics in some sense apply far below the infinite particle number limit.

The finite environment itself could simply be defined by a spectral structure of some hundred states. The most important fact is that the states are grouped into energy bands. Contrary to typical oscillator baths or the Jaynes-Cummings model the level splitting in the system coupled to the finite environment is not in resonance with the level splitting in the environment, but with the energy gap between those bands. This allows for a suitable energy transfer between system and reservoir. Furthermore, to describe a proper thermodynamical situation the density of states should in some sense increase exponentially with energy (for more details see [40]).

A finite environment which cannot be decomposed into uncoupled subunits any further may feature an arbitrary number of states in each band. For a rough first investigation one may think of a local environmental Hamiltonian with “bands” of degenerated levels. Thus, the respective system reservoir interaction leads to a broadening of the bands, keeping no further degeneracies for a random interaction. If the interaction remains weak the broadening of the band is, furthermore, not too strong (see [80]). For all complicated theoretical considerations it is often better to start without degeneracies directly, i.e. with a band of finite width. Thus, the respective local environmental Hamiltonian consists of bands with equidistant levels distributed over the whole band.

5.2. Beyond the Born Approximation

Recently, there have been some discussions whether the approximations applied in the derivation of the quantum master equation are also valid for finite environments. Especially, the finiteness and the change of the state of the environment within the decay time of the system could lead to a break down of mainly the Born approximation (the perturbation expansion in the coupling strength of the memory kernel of the Nakajima-Zwanzig equation, cf. Sect. 3.2).

It is a well-known fact that the short time behavior of the master equation is not a very good approximation, especially for non-Markovian systems. The stationary state remains to be correctly approximated (see [11]). This problem is mainly discussed under the term “non-Markovian quantum master equations” and could be overcome by using other techniques like the “time convolutionless method”¹ (TCL) in higher order to derive a proper approximated equation for such situations. Such a higher order TCL expansion is already beyond the standard Born approximation (second order approximation).

However, especially for such finite environments there have recently been some doubts about the correctness of the stationary state at all approached by the master equation (see Fig. 8.5). This even refers to the full Markovian case. Finally, this failure is a result of a non-converting TCL expansion for such finite environments (see [12]).

A hint for the background of the problem comes from quantum thermodynamics: in all investigations on the quantum mechanical foundation of the

¹In the seminar of theoretical physics in Stuttgart H.-P. Breuer stated in a talk on “Non-Markovian Quantum Master Equations” that TCL in higher order is a very good approximation also for the decay, whereas the standard second order Born approximated master equation is only suitable for the final stationary state.

second law according to quantum thermodynamics, entanglement plays a crucial role. The fact that all quantum master equations in Born approximation start from factorizing initial conditions, or even do not contain any possibility of entanglement between system and environment, becomes a major problem, especially for finite bath systems. Of course it is possible to treat also non-factorizing initial conditions by an open system approach, but this is practically unfeasible for any concrete environmental model (see [13] and Sect. 3.2). Maybe, by improving the TCL method using new projection operators as recently suggested by Breuer, it is possible to overcome the problem. However, a detailed discussion is beyond the scope of this text, therefore see [12, 39] and for some more intriguing phenomena in finite reservoir models see Sect. 8.3.

At least all these discussions underline the statement by Uhlenbeck cited at the beginning of Chap. 3 that even until now it is not completely clear what kind of Liouville equation a given quantum master equation really simulates. According to all of those difficulties let us present in the next Chapter yet another quantum thermodynamical method of analyzing a system coupled to a finite environment, the *Hilbert Space Average Method* (HAM) (see [38–40, 104]).

6. Hilbert Space Average Method

The most general demonstration of emergent classicality therefore consists of showing that, for a large collection of interacting particles described microscopically by quantum theory, the local densities become effectively classical.

J.J. Halliwell in [52]

The new method described in this Chapter is a method for investigating a small system S coupled to a very large, but finite environment E , called the *Hilbert Space Average Method* (HAM). As already mentioned we would like to end up with a closed equation for the system S . Thus, the environment enters by its influence on the system S only, not by some concrete dynamical variables. In order to deduce this closed equation the present approach relays on totally different approximation schemes than the projection operator technique does. Following Gemmer [36], we replace here some exact expectation values of the whole system (system and bath together) by a mean value in the respective Hilbert space compartment. Besides the dynamical equations for S , the theory provides some testable criteria for applicability. For a more detailed discussion of Hilbert space averages, see, e.g. [36, 38, 40].

6.1. Hamiltonian Model

The model we analyze is a two-level system S with state space \mathcal{H}_S . This system is coupled to a many-level system – the environment E . In contrast to standard environments consisting of an infinite number of, e.g. harmonic oscillators, this so called *finite environment* (state space \mathcal{H}_E) consists of two relevant bands¹ only featuring the same width and equidistant level spacing (see Fig. 6.1). The Hilbert space of the composite system is given by the

¹Note that the level spacing of S , unlike in typical oscillator baths or the Jaynes-Cummings Model, is not in resonance with the level spacing of the environment, but with the energy distance between the bands.

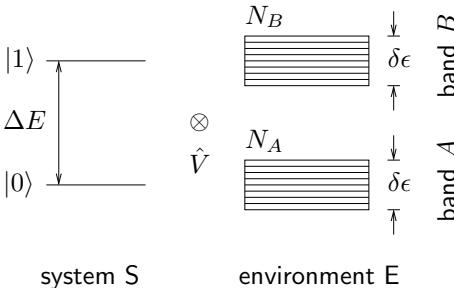


Figure 6.1.: Two-level system coupled to a finite environment. The spectrum of the environment deviates significantly from those of baths with infinitely many decoupled degrees of freedom.

tensor product $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_E$.

This type of finite environment may be viewed as a single molecule, a single quantum dot, an atom or simply a single harmonic oscillator. There are two principal differences of such a finite environment level scheme from the level scheme of, say, a standard oscillator bath: Firstly, the total amount of levels within a band may be finite and secondly there are several states for the lower band, i.e. the finite bath may feature arbitrary numbers of states in both bands. In contrast, the relevant bands of any infinite bath would consist of only one state in the lower and infinitely many states in the upper band.

For the respective model class we have found that the standard scheme, described in the last Chapters, namely the Born approximation², breaks down; only in the limit of an infinite bath the standard methods produce correct results [12, 39, 40]. This holds true even and especially in the limit of weak coupling and arbitrarily dense environmental spectra. Nevertheless, a statistical relaxation behavior can be induced by finite baths. This is not the behavior predicted by the standard methods. Thus, the principles of statistical mechanics in some sense apply below the infinite particle number limit. This also supports the concept of systems being driven towards equilibrium through increasing correlations with their environments [41, 93, 94, 127, 161] rather than the idea of system and environment remaining factorizable³ which is often attributed to the Born approximation [13, 154].

²In a vital discussion with M. Scully, F. Haake, G. Mahler and J. Gemmer at the FQMT Conference in Prague the author got the insight that several conditions for the applicability of standard open system techniques remain puzzling.

³The condition of factorizable initial conditions does not mean that system and bath will remain factorizable forever!

6.1.1. Projection and Transition Operators

Let us first introduce some useful projection respectively transition operators in both the system and the environmental Hilbert space. In \mathcal{H}_S we introduce standard operators $\hat{P}_{ij} = |i\rangle\langle j|$, where $|i\rangle$, $|j\rangle$ are energy eigenstates of the considered system S. As standard projection and transition operators the usual properties of such operators are met.

Furthermore, we define projection operators to the lower respectively upper band of the environment in \mathcal{H}_E by

$$\hat{\Pi}_a = \sum_{n_a} |n_a\rangle\langle n_a|. \quad (6.1)$$

Here and in the following the index n_a labels the levels of the a th energy band in the reservoir. For the concrete model shown in Fig. 6.1, we have defined the band indices, $a = A$ for the lower and $a = B$ for the upper band. Those operators meet the standard property

$$\hat{\Pi}_a \hat{\Pi}_{a'} = \delta_{aa'} \hat{\Pi}_{a'}. \quad (6.2)$$

Thus, the dimension of the respective subspace a is given by

$$N_a \equiv \text{Tr}\{\hat{\Pi}_a\}. \quad (6.3)$$

A set of important operators in the complete Hilbert space \mathcal{H} is defined by the combination of the above described operators in the separate Hilbert space compartments of system and reservoir, as

$$\hat{P}_{ij,a} = \hat{P}_{ij} \otimes \hat{\Pi}_a. \quad (6.4)$$

According to (6.2) we find

$$\hat{P}_{ij,a} \hat{P}_{i'j',a'} = \delta_{ji'} \delta_{aa'} \hat{P}_{ij',a'} \quad (6.5)$$

and thus the given operators form a group. One may easily convince oneself that

$$\text{Tr}\{\hat{P}_{ij,a}\} = \delta_{ij} N_a. \quad (6.6)$$

6.1.2. Canonical and Microcanonical Interaction

The total Schrödinger picture Hamiltonian of the model consists of a local and an interaction part

$$\hat{H} = \hat{H}_{\text{loc}} + \hat{V}, \quad (6.7)$$

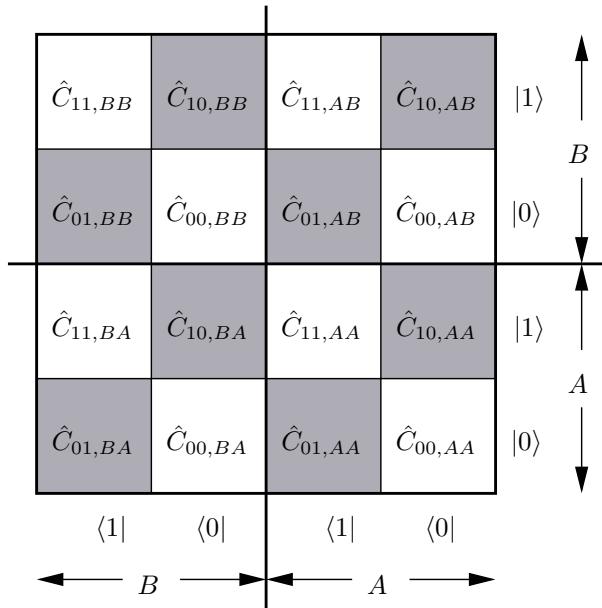


Figure 6.2.: Interaction matrix between system and environment, explanation see text.

where the local part reads

$$\hat{H}_{\text{loc}} = \hat{H}_S \otimes \hat{1}_E + \hat{1}_S \otimes \hat{H}_E. \quad (6.8)$$

For the special situation in Fig. 6.1 one may define

$$\hat{H}_S = \Delta E \hat{P}_{11}, \quad (6.9)$$

$$\hat{H}_E = \sum_{n_A} \frac{\delta \varepsilon n_A}{N_A} |n_A\rangle \langle n_A| + \sum_{n_B} \left(\Delta E + \frac{\delta \varepsilon n_B}{N_B} \right) |n_B\rangle \langle n_B|. \quad (6.10)$$

Note that $[\hat{\Pi}_a, \hat{H}_E] = 0$.

According to the transition respectively projection operators of S the complete interaction operator may be expanded as follows

$$\hat{V} = \sum_{ij} \hat{P}_{ij} \otimes \hat{C}_{ij} = \sum_{ij} \hat{P}_{ij} \otimes \sum_{ab} \hat{C}_{ij,ab} \quad (6.11)$$

with the environmental operators \hat{C}_{ij} . One may arrange the whole interaction Hamiltonian for the special model Fig. 6.1 according to Fig. 6.2. The coupling

strength $\lambda_{ij,ab}$ of a coupling block $\hat{C}_{ij,ab}$ is defined as the mean of the squared matrix elements

$$\lambda_{ij,ab}^2 := \frac{\text{Tr}_E\{\hat{C}_{ij,ab}\hat{C}_{ij,ab}^\dagger\}}{N_a N_b}. \quad (6.12)$$

According to the Hermiticity of the interaction we immediately find $\lambda_{ij,ab} = \lambda_{ji,ba}$. The system environment interactions are typically small compared to the local energies of (6.9) and (6.10) to model a proper thermodynamical situation.

Here, the interaction between system and environment essentially consists of both a coupling that induces transitions inside the system ($i \neq j$) as well as one that keeps the state of the system unchanged, but couples some levels in the environment ($i = j$). Since the first one is able to exchange energy between system and environment it is sometimes called canonical coupling \hat{V}_{can} . The second one just produces some entanglement, but does not exchange energy and therefore refers to a microcanonical⁴ coupling \hat{V}_{mic} . In Fig. 6.2 interaction matrix blocks belonging to the canonical coupling are painted gray, the microcanonical ones white. Eventually, we split the complete interaction Hamiltonian into two operators, the canonical and the microcanonical part

$$\hat{V} = \hat{V}_{\text{can}} + \hat{V}_{\text{mic}}. \quad (6.13)$$

Instead of the separate definition of the interaction strength on each subspace (cf. (6.12)), one may define in such a situation the overall canonical λ_{can} and the overall microcanonical λ_{mic} interaction strength for all gray respectively white blocks of Fig. 6.2 together.

We do not specify the interaction in more detail here. For all theoretical considerations we only need two further conditions concerning the interaction matrix. First we claim that the different interaction matrices displayed in Fig. 6.2 are not correlated unless they refer to parts of the interaction which are adjoints of each other

$$\text{Tr}_E\{\hat{C}_{ij,ab}\hat{C}_{j'i'b'a'}\} = \lambda_{ij,ab}^2 N_a N_b \delta_{ii'} \delta_{jj'} \delta_{aa'} \delta_{bb'} \quad (6.14)$$

(e.g. no correlation between $\hat{C}_{11,BB}$ and $\hat{C}_{00,BB}$ etc.). Furthermore, we need the condition that the partial environmental traces over parts of the interac-

⁴A microcanonical reservoir coupling only appears within Quantum Thermodynamics (cf. [40]). Here, entanglement between system and reservoir is crucial for any thermodynamical behavior. This is a coupling type which only produces entanglement without exchanging energy.

tion vanish

$$\text{Tr}_E \{ \hat{C}_{ij,aa} \hat{\Pi}_a \} = 0, \quad (6.15)$$

$$\text{Tr}_E \{ \hat{C}_{ii,aa} \hat{\Pi}_b \} = 0, \quad (6.16)$$

with arbitrary b . Both constraints are not too strong conditions on the interaction and definitely apply for the numerical examples studied.

6.1.3. Dyson Short Time Dynamics

The complete time evolution of system and environment is governed by the full system Schrödinger equation. Transforming the model Hamiltonian of Sect. 6.1.2 to the interaction picture, \hat{V} itself gains a time dependence

$$\hat{V}(t) = e^{i\hat{H}_{\text{loc}}t/\hbar} \hat{V} e^{-i\hat{H}_{\text{loc}}t/\hbar}. \quad (6.17)$$

However, those unitary time evolution operators are product operators due to the local Hamiltonian (6.8). Thus we get

$$\begin{aligned} \hat{V}(t) &= \sum_{ij} e^{i\hat{H}_{\text{loc}}t/\hbar} \hat{P}_{ij} \otimes \hat{C}_{ij} e^{-i\hat{H}_{\text{loc}}t/\hbar} \\ &= \sum_{ij} e^{i\hat{H}_S t/\hbar} |i\rangle\langle j| e^{-i\hat{H}_S t/\hbar} e^{i\hat{H}_E t/\hbar} \hat{C}_{ij} e^{-i\hat{H}_E t/\hbar} \\ &= \sum_{ij} e^{i\omega_{ij} t} \hat{P}_{ij} e^{i\hat{H}_E t/\hbar} \hat{C}_{ij} e^{-i\hat{H}_E t/\hbar}, \end{aligned} \quad (6.18)$$

with the frequencies

$$\omega_{ij} \equiv \frac{E_i - E_j}{\hbar}, \quad (6.19)$$

defined according to the system energy eigenvalues E_i . Defining the new Dirac picture environmental interaction operators

$$\hat{C}_{ij}(t) = e^{i\omega_{ij} t} e^{i\hat{H}_E t/\hbar} \hat{C}_{ij} e^{-i\hat{H}_E t/\hbar}, \quad (6.20)$$

one finds

$$\hat{V}(t) = \sum_{ij} \hat{P}_{ij} \otimes \hat{C}_{ij}(t). \quad (6.21)$$

Thus, neither the special structure of the interaction (cf. Fig. 6.2) nor the mentioned additional conditions are changed by the transformation to the interaction picture.

Instead of following the complete time evolution of the system in the interaction picture governed by the time-dependent interaction Hamiltonian $\hat{V}(t)$, we concentrate on a short time step τ . Thus, we perform a Dyson expansion (von-Neumann expansion) of the Schrödinger equation in the interaction picture

$$|\psi(\tau)\rangle = \hat{D}(\tau) |\psi(0)\rangle , \quad (6.22)$$

with

$$\hat{D}(\tau) = \hat{1} + \sum_{j=1}^{\infty} \left(-\frac{i}{\hbar} \right)^j \hat{U}_j(\tau) \quad (6.23)$$

and the standard text book time ordered integrals

$$\hat{U}_j(\tau) = \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \dots \int_0^{\tau^{j-1}} d\tau^j \hat{V}(\tau') \hat{V}(\tau'') \dots \hat{V}(\tau^j) \quad (6.24)$$

over the interaction operators (see [134]). In case of a weak system environment interaction, (6.23) can be truncated at second order. For a small time step τ this series expansion yields

$$|\psi(\tau)\rangle \approx \left[\hat{1} - \frac{i}{\hbar} \hat{U}_1(\tau) - \frac{1}{\hbar^2} \hat{U}_2(\tau) \right] |\psi(0)\rangle , \quad (6.25)$$

with the two time evolution operators⁵

$$\hat{U}_1(\tau) = \int_0^\tau d\tau' \hat{V}(\tau') , \quad (6.26)$$

$$\hat{U}_2(\tau) = \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \hat{V}(\tau') \hat{V}(\tau'') . \quad (6.27)$$

In contrast to the second order, the first order operator $\hat{U}_1(\tau)$ is Hermitian due to the Hermiticity of the interaction.

Since we have to require that the time evolution operator is a suitable unitary operator (conservation of normalization), we state that

$$\begin{aligned} \hat{D}^\dagger \hat{D} &\stackrel{!}{=} \hat{1} \\ &= (\hat{1} + \frac{i}{\hbar} \hat{U}_1 - \frac{1}{\hbar^2} \hat{U}_2^\dagger) (\hat{1} - \frac{i}{\hbar} \hat{U}_1 - \frac{1}{\hbar^2} \hat{U}_2) \\ &\approx \hat{1} + \frac{1}{\hbar^2} (\hat{U}_1^2 - \hat{U}_2^\dagger - \hat{U}_2) , \end{aligned} \quad (6.28)$$

⁵Note that the integration in (6.27) is time ordered, i.e. $\tau \geq \tau' \geq \tau'' \geq 0$

again approximated to second order. Therefore, all higher orders have to vanish and thus we find the following additional condition

$$\hat{U}_2^\dagger + \hat{U}_2 = \hat{U}_1^2. \quad (6.29)$$

6.1.4. Reduced Dyson Short Time Dynamics

Since we are mainly interested in the time evolution of the system S separately, we have to account for its reduced density operator out of the pure state $|\psi(t)\rangle$ of the full system. For this task it is useful to consider the set of operators introduced in (6.4), corresponding to elements of the reduced density operator of the considered system and the occupation probability of “energy bands” of the environment. Let the expectation value of the projector (6.4) be denoted as

$$\langle\psi|\hat{P}_{ij,a}|\psi\rangle \equiv P_{ij,a}. \quad (6.30)$$

Consequently, the reduced density matrix elements ρ_{ij} read

$$\rho_{ij} = \sum_a P_{ij,a}. \quad (6.31)$$

This is nothing but the partial trace over the environmental degrees of freedom, leading to the reduced density matrix elements of the system.

The short time evolution of the expectation value $P_{ij,a}$ yields

$$P_{ij,a}(\tau) \equiv \langle\psi(\tau)|\hat{P}_{ij,a}|\psi(\tau)\rangle. \quad (6.32)$$

Having derived a dynamical equation for these expectation values the respective time evolution of the reduced density matrix elements is given by (6.31). Using the short time dynamics (6.22) one finds

$$P_{ij,a}(\tau) = \langle\psi|\hat{D}^\dagger \hat{P}_{ij,a} \hat{D}|\psi\rangle \equiv \langle\psi|\hat{S}|\psi\rangle, \quad (6.33)$$

where we skipped the explicit notation of the time dependence of the Dyson time evolution operators and, furthermore, have introduced the shorthand $|\psi(0)\rangle \equiv |\psi\rangle$ and the operator $\hat{S} \equiv \hat{D}^\dagger \hat{P}_{ij,a} \hat{D}$.

Since the right hand side of (6.33) is a complicated function of the time evolution concerning the full system, we need an approximation scheme to evaluate this term without following the whole dynamics. It turns out that the Hilbert space average method (HAM) is good candidate to reach a suitable guess for the right hand side.

6.2. Hilbert Space Average

In this Section we will present the definition and application of the Hilbert space average method on the given model system, following Gemmer. For more details about Hilbert space averages see [40].

6.2.1. Definition of the Hilbert Space Average

The Hilbert space average method (HAM) is, in essence, a technique to produce guesses for the values of quantities defined as functions of a wave function $|\psi\rangle$ while $|\psi\rangle$ itself is not known in full detail, only some features of it. In particular it will produce a guess for the expectation value $\langle\psi|\hat{S}|\psi\rangle$ [cf. (6.33)] if the only information about $|\psi\rangle$ is a set of initial expectation values $\langle\psi|\hat{P}_{ij,a}|\psi\rangle = P_{ij,a}$. Naturally, such a statement has to be a guess only since there are many different $|\psi\rangle$, in general, that are in accord with the given set of $P_{ij,a}$, but possibly produce different values for $\langle\psi|\hat{S}|\psi\rangle$. The question here is whether the distribution of $\langle\psi|\hat{S}|\psi\rangle$'s produced by the respective set of $|\psi\rangle$'s is broad or whether almost all those $|\psi\rangle$'s yield $\langle\psi|\hat{S}|\psi\rangle$'s that are approximately equal. It turns out that if the spectral width of \hat{S} is not too large and \hat{S} is high-dimensional, almost all individual $|\psi\rangle$ yield an expectation value close to the mean of the distribution of $\langle\psi|\hat{S}|\psi\rangle$'s [40]. To find that mean one has to average with respect to the $|\psi\rangle$'s. We call this a Hilbert space average S and denote it as

$$S = \llbracket \langle\psi|\hat{S}|\psi\rangle \rrbracket_{\{\langle\psi|\hat{P}_{ij,a}|\psi\rangle = P_{ij,a}\}}. \quad (6.34)$$

This expression stands for the average of $\langle\psi|\hat{S}|\psi\rangle$ over all $|\psi\rangle$ that feature $\langle\psi|\hat{P}_{ij,a}|\psi\rangle = P_{ij,a}$, but are uniformly distributed otherwise. Uniformly distributed means invariant with respect to all unitary transformations that leave $\langle\psi|\hat{P}_{ij,a}|\psi\rangle = P_{ij,a}$ unchanged, i.e. also S remains invariant under the respective transformations.

6.2.2. Approximation Scheme

With the definition of an expectation value according to a density operator, we find

$$S = \llbracket \langle\psi|\hat{S}|\psi\rangle \rrbracket = \llbracket \text{Tr}\{\hat{S}|\psi\rangle\langle\psi|\} \rrbracket, \quad (6.35)$$

where we skip the constraints (constant expectation values) of the Hilbert space average for the moment. Exchanging the average and the trace operation

one may rewrite

$$S = \text{Tr}\{\hat{S}[\![\psi]\langle\psi]\!]\} \equiv \text{Tr}\{\hat{S}\hat{\alpha}\} \quad (6.36)$$

with

$$\hat{\alpha} \equiv [\![\psi]\langle\psi]\!]_{\{\langle\psi|\hat{P}_{ij,a}|\psi\rangle = P_{ij,a}\}}. \quad (6.37)$$

Instead of computing this Hilbert space average $\hat{\alpha}$ directly as done, e.g. in Ref. [38, 40] we will proceed in a slightly different way here. Any unitary transformation leaves $\langle\psi|\hat{P}_{ij,a}|\psi\rangle = P_{ij,a}$ invariant. Therefore, the respective transformation has to leave $\hat{\alpha}$ invariant, too, i.e.

$$e^{i\hat{G}}\hat{\alpha}e^{-i\hat{G}} = \hat{\alpha} \quad \text{with} \quad [\hat{G}, \hat{P}_{ij,a}] = 0. \quad (6.38)$$

This, however, can only be fulfilled if $[\hat{G}, \hat{\alpha}] = 0$. Since the projection operators $\hat{P}_{ij,a}$ form a complete basis one may expand the Hilbert space average into this basis finding

$$\hat{\alpha} = \sum_{ija} p_{ij,a} \hat{P}_{ij,a} \quad (6.39)$$

with the expansion coefficients $p_{ij,a}$. In principle there could be addends of higher order, e.g. squares of the operators, but according to the properties of the projection and transition operators, those terms are already contained. This results, since the set of operators $\hat{P}_{ij,a}$ form a group (cf. (6.5)).

Furthermore, one has to fulfill the condition

$$P_{i'j',a'} = \text{Tr}\{\hat{P}_{i'j',a'}\hat{\alpha}\} \quad (6.40)$$

due to the definition of $\hat{\alpha}$ (6.36) and (6.37). Plugging (6.39) into (6.40) one obtains

$$P_{i'j',a'} = \sum_{ija} p_{ij,a} \text{Tr}\{\hat{P}_{i'j',a'}\hat{P}_{ij,a}\} \quad (6.41)$$

from which the $p_{ij,a}$ may be determined. It is not obvious, but a straightforward calculation to find

$$p_{ij,a} = \frac{P_{ji,a}}{N_a}, \quad (6.42)$$

where we use (6.2) and (6.5). Thus, the construction of a given Hilbert space average is defined with the help of (6.39), (6.42), and (6.36), finally, resulting in

$$S = \text{Tr}\{\hat{S}\hat{\alpha}\} = \sum_{ija} \frac{P_{ji,a}}{N_a} \text{Tr}\{\hat{S}\hat{P}_{ij,a}\}. \quad (6.43)$$

6.2.3. Hilbert Space Averaged Time Evolution

In the following we will use the Hilbert space average (6.43) to simplify the interesting time evolution equation (6.33), yielding

$$\begin{aligned} P_{ij,a}(\tau) &= \langle \psi | \hat{S} | \psi \rangle = \text{Tr}\{\hat{S}|\psi\rangle\langle\psi|\} \\ &\approx \text{Tr}\{\hat{S}\hat{\alpha}\} = S . \end{aligned} \quad (6.44)$$

Using the Hilbert space average (6.43) calculated in the last Section and reintroducing the operator $\hat{S} \equiv \hat{D}^\dagger \hat{P}_{ij,a} \hat{D}$ we find

$$P_{ij,a}(\tau) \approx \sum_{i'j'a'} \frac{P_{j'i',a'}}{N_{a'}} \text{Tr}\{\hat{D}^\dagger \hat{P}_{ij,a} \hat{D} \hat{P}_{i'j',a'}\} . \quad (6.45)$$

It remains to analyze the traces on the right hand side of this equation. This term is abbreviated by \bar{S} . In a suitable second order approximation of the time evolution operator \hat{D} we get (omitting immediately all terms of higher than second order)

$$\begin{aligned} \bar{S} &= \text{Tr}\{\hat{D}^\dagger \hat{P}_{ij,a} \hat{D} \hat{P}_{i'j',a'}\} = \\ &\text{Tr}\left\{\left(\hat{P}_{ij,a} + \frac{i}{\hbar} \hat{U}_1 \hat{P}_{ij,a} - \frac{i}{\hbar} \hat{P}_{ij,a} \hat{U}_1 + \frac{1}{\hbar^2} \hat{U}_1 \hat{P}_{ij,a} \hat{U}_1 \right.\right. \\ &\quad \left.\left.- \frac{1}{\hbar^2} \hat{U}_2^\dagger \hat{P}_{ij,a} - \frac{1}{\hbar^2} \hat{P}_{ij,a} \hat{U}_2\right)\hat{P}_{i'j',a'}\right\}, \end{aligned} \quad (6.46)$$

where we use the Hermiticity of the operator \hat{U}_1 . Since the concrete calculation of this expression contains lots of algebra and no new insight, it has been shifted to App. A.

An important fact is that the above trace relation mainly depends on the *integrated environmental correlation function* defined as

$$f_{ij,ab}(\tau) := 2 \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}_E\{\hat{C}_{ij}(\tau'') \hat{\Pi}_b \hat{C}_{ji} \hat{\Pi}_a\} . \quad (6.47)$$

Those functions are essentially integrals over the same environmental temporal correlation functions that appear in the memory kernels of standard projection operator techniques. But here they explicitly correspond to transitions between different energy subspaces of the environment.

So far we have approximated the complicated time evolution of those expectation values by the Hilbert space average method. Using those results we will derive a proper set of dynamical equations for the system S in the next Chapter.

7. General HAM Rate Equation

We call dynamical laws reversible if any process following this dynamics is changed into a possible process by a time reversal. In thermodynamics we know processes which do not possess this property. They are irreversible.

F. Schlögl in [130]

In the last Chapter we have applied the new *Hilbert Space Average Method* (HAM) to our actual model system – a small system coupled to a finite environment. Besides a second order Dyson expansion of the Schrödinger equation we have performed an average in the Hilbert space of the complete system. The aim of the investigation was to find a closed dynamical equation exclusively for some quantities of the system S. The approximation scheme results in (6.45) and especially (6.46). The concrete evaluation of (6.46) in App. A yields (cf. (A.2), (A.5) and (A.20))

$$\bar{S} = \delta_{i'j}\delta_{j'i}\delta_{a'a}N_a + \frac{1}{\hbar^2} \left(\delta_{ij} \delta_{i'j'} \text{Ref}_{ii',aa'}(\tau) - \frac{1}{2} \sum_{mb} \delta_{j'i} \delta_{ji'} \delta_{a'a} [f_{im,a'b}(\tau) + f_{jm,a'b}^*(\tau)] \right). \quad (7.1)$$

Using this result we can derive the most general form of a rate equation for the investigated model situation in the following. Furthermore, we examine the validity of the approximations of the last Chapter and investigate the limits to the applicability of HAM.

7.1. Short Time Iteration Scheme

The short time evolution equation of the expectation value (6.45) reads

$$P_{ij,a}(\tau) \approx \sum_{i'j'a'} \frac{P_{j'i',a'}}{N_{a'}} \bar{S}. \quad (7.2)$$

Plugging in (7.1) we finally get

$$\begin{aligned} P_{ij,a}(\tau) &= P_{ij,a} + \frac{1}{\hbar^2} \sum_{i'a'} \delta_{ij} \frac{P_{i'i',a'}}{N_{a'}} \text{Ref}_{i'i',aa'}(\tau) \\ &\quad - \frac{1}{2\hbar^2} \sum_{mb} \frac{P_{ij,a}}{N_a} [f_{im,ab}(\tau) + f_{jm,ab}^*(\tau)]. \end{aligned} \quad (7.3)$$

Remember that all expectation values $P_{ij,a}$ refer to the initial time. Instead of using the initial time zero we will choose an arbitrary initial time t . This yields for the expectation values corresponding to diagonal elements ($i = j$)

$$\begin{aligned} P_{ii,a}(t + \tau) &= \\ P_{ii,a}(t) + \frac{1}{\hbar^2} \sum_{mb} \text{Ref}_{im,ab}(\tau) &\left[\frac{P_{mm,b}(t)}{N_b} - \frac{P_{ii,a}(t)}{N_a} \right], \end{aligned} \quad (7.4)$$

where we use the fact that $f_{im,ab} + f_{im,ab}^* = 2\text{Ref}_{im,ab}$. For the expectation values corresponding to off-diagonal elements ($i \neq j$) we get

$$\begin{aligned} P_{ij,a}(t + \tau) &= \\ P_{ij,a}(t) - \frac{1}{2\hbar^2} \frac{P_{ij,a}(t)}{N_a} \sum_{mb} &[f_{im,ab}(\tau) + f_{jm,ab}^*(\tau)]. \end{aligned} \quad (7.5)$$

Since we will primarily analyze the squared absolute value of the off-diagonal elements, we consider

$$\begin{aligned} |P_{ij,a}(t + \tau)|^2 &= |P_{ij,a}(t)|^2 |1 + c|^2 \\ &= |P_{ij,a}(t)|^2 (1 + c + c^* + cc^*) \end{aligned} \quad (7.6)$$

with a complex number c containing the above sum over correlation functions. The last term cc^* contains products of correlation functions and is thus of higher than second order in the interaction. Since the time evolution is a second order approximation, we skip this term finding

$$\begin{aligned} |P_{ij,a}(t + \tau)|^2 &= \\ |P_{ij,a}(t)|^2 - \frac{1}{\hbar^2} \frac{|P_{ij,a}(t)|^2}{N_a} \sum_{mb} &[\text{Ref}_{im,ab}(\tau) + \text{Ref}_{jm,ab}(\tau)]. \end{aligned} \quad (7.7)$$

One may account for the environmental correlation functions by directly integrating the interaction operator of a concrete model system according to (6.47). However, we routinely use an approximation for those integrals in terms of Fermi's Golden Rule. Before we proceed with such an approximation in the next Chapter let us first derive the most general set of differential equations, describing the dynamics of the discussed model system.

7.2. Closed Differential Equation

We start with the consideration of the real part of the integrated correlation function $f_{im,ab}$ in (7.4) and (7.5). The integrated correlation function $f_{im,ab}$ is given by (6.47). The integrand of (6.47) typically features short decay times τ_c compared to the system dynamics. After the corresponding decay time τ_c , the integration in (6.47) leads to a linear function in time. That such a linear behavior in time can indeed be found will be discussed in Sect. 7.3 (see also Chap. 8). Thus, for $\tau > \tau_c$ the real part of the integrated correlation function (6.47) may be expressed as

$$\text{Re}f_{im,ab}(\tau) \approx \gamma_{im,ab} N_b \tau, \quad (7.8)$$

with the time independent $\gamma_{im,ab}$, called rates. However, note that all rates $\gamma_{im,ab}$ which do not belong to adjoint parts of the interaction vanish like already $f_{im,ab}$ does (see Sect. 6.1.2). Especially those rates will only be nonzero for $E_i - E_m \approx E_a - E_b$ since otherwise the correlation function rapidly oscillates before it decays and hence the corresponding integrals vanish. This also refers to the total energy conservation in the model – a non-resonant transition is extremely improbable. Furthermore, such rates typically depend on the state densities in the final band and, thus, respective “forward” and “backward” rates are, for equal band widths, connected as

$$\gamma_{im,ab} = \frac{N_a}{N_b} \gamma_{mi,ba}. \quad (7.9)$$

We assume that the decay times τ_c of the correlation functions are indeed small compared to the resulting decay times of the system¹. Thus, inserting (7.8) into Eqs. (7.4) and (7.7), and furthermore using (7.9) yields

$$\frac{P_{ii,a}(t + \tau) - P_{ii,a}(t)}{\tau} = \sum_{mb} \frac{\gamma_{im,ab}}{\hbar^2} \left(P_{mm,b}(t) - \frac{N_b}{N_a} P_{ii,a}(t) \right) \quad (7.10)$$

$$\frac{|P_{ij,a}(t + \tau)|^2 - |P_{ij,a}(t)|^2}{\tau} = - \frac{|P_{ij,a}(t)|^2}{\hbar^2} \sum_{mb} (\gamma_{mi,ba} + \gamma_{mj,ba}). \quad (7.11)$$

Iterating this short time evolution scheme (7.10) and (7.11), i.e. taking the $P_{ij,a}(t + \tau)$ for the $P_{ij,a}(t)$ of the next step, allows for a stepwise computation of the evolution of the $P_{ij,a}$'s. For small τ one can transform this iteration

¹That such a separation of time scales is indeed plausible will be investigated in Sect. 7.3. Furthermore, an example is given in Chap. 8.

scheme into a set of differential equations

$$\frac{d}{dt}P_{ii,a}(t) = \frac{1}{\hbar^2} \sum_{mb} \gamma_{im,ab} \left(P_{mm,b}(t) - \frac{N_b}{N_a} P_{ii,a}(t) \right), \quad (7.12)$$

$$\frac{d}{dt}|P_{ij,a}(t)|^2 = -\frac{1}{\hbar^2}|P_{ij,a}(t)|^2 \sum_{mb} (\gamma_{mi,ba} + \gamma_{mj,ba}). \quad (7.13)$$

According to (6.31), the $P_{ij,a}$'s determine the local state of the considered quantum system completely. The result is, of course, just like HAM itself, only a best guess, but for appropriate systems this guess can be rather accurate.

Summing over the band index a in (7.12) and (7.13) one would finally get the differential equation for the elements of the reduced density operator, cf. (6.31). However, it is not possible to derive a closed set of differential equations for those quantities in general. It turns out that only for some special model systems and classes of initial states such a closed description is feasible. Because of this lack of a suitable set of dynamical equations on the basis of the elements of the density operator and the dependence on the initial state, a discussion about the Markovity of the model system has been invoked. A model is usually called Markovian in case it forgets its respective initial conditions. Obviously, this does not seem to be the case here since the initial states play a crucial role for the dynamical equation. However, in contrast to the dependence on initial conditions, all environmental correlation functions are decaying very fast, which is sometimes also discussed in connection with Markovity.

Despite the fact that there is no closed equation for the density matrix elements, in general, the equation on the basis of the expectation values is closed. Solving those equations opens the possibility to get a complete solution for the reduced density matrix elements, too. Thus, we are able to guess the behavior of the respective model class – a system coupled to a finite environment – according to the new *Hilbert Space Average Method (HAM)*.

Furthermore, even in the special case where a closed equation for the state of the system is possible, those differential equations are eventually different from the textbook dynamics one would have gotten by the standard projection operator techniques. A detailed comparison with the standard result is beyond the scope of this text. We refer the interested reader to [12, 13].

In the remaining Chapters of this Part, we will discuss some of the special model systems in more detail. We will especially concentrate on thermalization and decoherence models, where a closed description on the basis of the elements of the reduced density matrix is feasible. But, let us first investigate the applicability of HAM in the next Section.

7.3. Limits of Applicability

Those dynamical considerations of the last Sections are only a guess, but as a guess they are valid for any initial state regardless of whether it is pure, correlated, entangled, etc., in contrast to the standard Nakajima-Zwanzig and TCL methods. HAM allows for a direct prediction of the typical behavior of the system. Nevertheless, for deriving the above HAM rate equations we have used several approximations: The truncation of the Dyson series in second order (see (6.25)), the replacement of the actual value of an expectation value by the average in the respective Hilbert space compartment (see (6.44)) and the assumption that the integrated environmental correlation functions grow linearly in τ (see (7.8)). In the following we will investigate the validity of these approximations in more detail.

7.3.1. Decay of Environmental Correlations

In Sect. 7.2 (cf. (7.8)) we have used the assumption that the integral over the environmental correlation function would grow linearly in τ . For this approximation to be valid, we have to require that the correlation function defined by (cf. (6.47))

$$g(t) = \text{Tr}_E\{\hat{C}_{ij}(t)\hat{\Pi}_b\hat{C}_{ji}\hat{\Pi}_a\} \quad (7.14)$$

decays quite fast. Let the time scale on which these correlations typically decay be τ_c . Only for times $\tau \gg \tau_c$ the respective approximation is justified, which is sometimes referred to as the Markov assumption. To roughly estimate this correlation time τ_c we investigate the Fourier transform of the above correlation function

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} g(t). \quad (7.15)$$

Calling the width of the spectrum of this Fourier transform $\Delta\omega$ we may use this as the respective time scale on which the above correlations decay

$$\tau_c \approx \frac{2\pi}{\Delta\omega}. \quad (7.16)$$

The above correlation function refers to a transition in the system between state i and j and from band b to band a in the environment. As already mentioned, energy conservation claims that $E_i - E_j \approx E_b - E_a$, where the energy splitting in the system corresponds to a transition between middle levels of the bands in the environment. However, a transition from the highest level of the

upper band to the lowest level in the lower band leads to a maximum energy displacement $\hbar\Delta\omega$ compared to the mean energy of the whole transition. This maximum displacement is approximately given by the sum of widths of the two involved bands in the environment. Using bands of the same width $\delta\epsilon$ we get for the decay time of correlations in the environment

$$\hbar\Delta\omega \approx 2\delta\epsilon \quad \text{thus} \quad \tau \gg \tau_c \approx \frac{\pi\hbar}{\delta\epsilon}. \quad (7.17)$$

Obviously, τ_c only depends on the width of the bands in the environment. Thus the linear regime, where the approximation (7.8) is justified, is reached after a time τ_c . As long as this linear regime is reached before other approximations fail the respective approximation is valid.

Note that the above correlation function contains a revival time for finite systems (cf. [13]), but typically this time is very large compared to the above decay time (see [42]).

7.3.2. Truncation of the Dyson Series

In (6.25) we have used a second order truncation of the Dyson series which is a reasonably good approximation for short times τ and a small interaction strength. Introducing the time scale on which this approximation breaks down by τ_D , we have to require that $\tau \ll \tau_D$.

We consider the time dependence of the expectation value, again in second order approximation of the Dyson series

$$\langle \psi(\tau) | \psi(\tau) \rangle = \langle \psi(0) | \hat{D}_2^\dagger \hat{D}_2 | \psi(0) \rangle. \quad (7.18)$$

The second order approximation is only suitable if the second order terms according to (6.25) are already small compared to the lower orders. In the following we use as an initial state $\hat{\rho}_0 \equiv |\psi(0)\rangle\langle\psi(0)|$. From (6.29) we know that the different second order terms are equivalent. Therefore, we concentrate on the term

$$\begin{aligned} f(\tau) &= \text{Tr}\{\hat{\rho}_0 \hat{U}_1^2(\tau)\} \\ &= \int_0^\tau d\tau' \int_0^\tau d\tau'' \text{Tr}\{\hat{\rho}_0 \hat{V}(\tau') \hat{V}(\tau'')\}, \end{aligned} \quad (7.19)$$

as the error resulting from the second order approximation. As long as this term remains small compared to lower orders (zeroth order, since the first order vanishes completely), the respective approximation is justified. Since the zeroth order refers to the normalization of the state $|\psi(\tau)\rangle$ we require

$f(\tau) \ll 1$. The above integral can be transformed to a time ordered integral (see App. A and especially (A.15)-(A.18)), finding

$$f(\tau) = 2\text{Re} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}\{\hat{\rho}_0 \hat{V}(\tau'') \hat{V}\}. \quad (7.20)$$

Obviously, the error (7.19) contains the respective initial state $\hat{\rho}_0$ of system and environment. For a very rough estimate of the time scale on which the second order expansion is valid, we use some central features of this initial state. Thus, instead of using $\hat{\rho}_0$ in full detail we introduce the test state

$$\hat{\rho}'_0 = \sum_{ia} \rho_{ii,aa} \hat{P}_{ii,a} \quad \text{with} \quad \rho_{ii,aa} = \text{Tr}\{\hat{\rho}_0 \hat{P}_{ii,a}\}, \quad (7.21)$$

featuring the same occupation numbers of both levels in the system and bands in the environment as the correct initial state $\hat{\rho}_0$. However, apart from that it is diagonal (no correlations). Furthermore, the levels inside a band are equally occupied (small band width approximation). To gain this special test state $\hat{\rho}'_0$ we use the information about the occupation of different energy subspaces of the complete model and skip the rest. Since energy conservation is given for the described dynamics of the system, only energy conserving transitions are allowed, i.e. we restrict ourselves to an energy subspace by our choice of the respective initial state. This again refers to the above mentioned occupation probabilities.

Plugging in the test state (7.21) and the interaction (6.21) into (7.20) we get

$$f(\tau) = 2\text{Re} \sum_{ija} \rho_{ii,aa} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}_E\{\hat{C}_{ij}(\tau'') \hat{C}_{ji} \hat{\Pi}_a\}. \quad (7.22)$$

Realizing that diagonal elements of the density operator are real and introducing the unit operator of the environment in terms of projection operators and using the definition (6.47) we find

$$\begin{aligned} f(\tau) &= 2 \sum_{ijab} \rho_{ii,aa} \text{Re} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}_E\{\hat{C}_{ij}(\tau'') \hat{\Pi}_b \hat{C}_{ji} \hat{\Pi}_a\} \\ &= 2 \sum_{ijab} \rho_{ii,aa} \text{Re} f_{ij,ab}. \end{aligned} \quad (7.23)$$

As stated before at the beginning of Chap. 7.2, those integrals increase linearly with time (after the decay time τ_c). Thus, together with (7.8) we find

$$f(\tau) \approx 2 \sum_{ij,ab} \rho_{ii,aa} \gamma_{ij,ab} N_b \tau \equiv \Gamma \tau, \quad (7.24)$$

where again the summation is restricted by the side condition $E_i - E_j \approx E_a - E_b$. The coefficient $\rho_{ii,aa}$ refers to the selected initial energy distribution in the system and thus determines the respective energy subspace to which the dynamics is restricted.

A time for which the second order approximation definitely fails is the time τ_D for which $f(\tau_D) \approx 1$. This is the case for the time

$$\tau \ll \tau_D \approx \frac{1}{\Gamma}, \quad (7.25)$$

which obviously depends on all the possible rates and therefore on the coupling strength of system and environment as well as on the sizes of respective bands and the chosen energy subspace.

Having established a concrete model situation and chosen an initial energy subspace, one could check whether these conditions (the short and the long time approximation) discussed in the last Sections are met in the sense that

$$\tau_c \ll \tau \ll \tau_D, \quad (7.26)$$

thus $\tau_c \ll \tau_D$. If those conditions are indeed fulfilled, the system will behave statistically, eventually following the derived rate equation at least in the chosen energy subspace.

7.3.3. Hilbert Space Variance

We have approximated time dependent expectation values by an average over a respective set of states in the Hilbert space compartment featuring the same initial expectation values. This is only a reasonable approximation if each of the states out of the respective set already features nearly the same expectation value as the mean. In other words, the landscape of this expectation value over the respective Hilbert space region has to be very flat. To investigate this landscape we consider the Hilbert space variance of the respective quantity Δ_H (cf. Sect. 6.2). Those are the Hilbert space variances of expectation values of Hermitian operators, here the second order terms of the time evolution operators, e.g. \hat{U}_1^2 . For any such object, we have evaluated the Hilbert space variance in App. D (cf. [40]) finding

$$\Delta_H = \frac{1}{N_a + 1} \left[\frac{\text{Tr}\{\hat{U}_1^4\}}{N_a} - \left(\frac{\text{Tr}\{\hat{U}_1^2\}}{N_a} \right)^2 \right]. \quad (7.27)$$

This is obviously the square of the spectral variance divided by the respective dimension N_a of the Hilbert space compartment. We thus claim that as long as the spectral variance of the interaction remains small the approximation is indeed applicable.

8. Thermalization

...environmental induced decoherence is omnipresent in the microscopic world. It is found, e.g., for an atom confined in a quantum optical trap, or for electron propagation in a mesoscopic device.

U. Weiss in [154]

The considerations in the last Chapter refer to both the decay of diagonal elements of the density operator of the system into a Boltzmann distribution and the decoherence, i.e. the disappearance of off-diagonal elements. In the following we will investigate the decay of diagonal elements of the reduced density operator in absence of any explicit off-diagonal damping. This means that we neglect parts of the interaction which only lead to an intra-band relaxation in the environment (referring to all white parts in Fig. 6.2). However, this does not mean that there is no damping of off-diagonal elements in the reduced density matrix at all. But, the off-diagonal decay is strictly bound to the thermalization within the system, since energy exchange between two systems also leads to local decoherence.

8.1. Damping Model

The energy scheme of system and environment is just the same as in the previous investigation (see Fig. 6.1). However, instead of using the whole complicated model Hamiltonian as sketched in Fig. 6.2, we investigate a reduced model. Besides providing better understanding of the theoretical concepts behind HAM, there are some more advantages of the reduced model: Firstly, the model opens the possibility of writing down a closed equation for the density matrix elements of the system, at least if restricting oneself to some concrete energy subspaces. Secondly, it is possible to directly integrate in such models the complete Schrödinger equation of system and bath together. This also opens the possibility of investigating the quality of the approximations due to HAM.

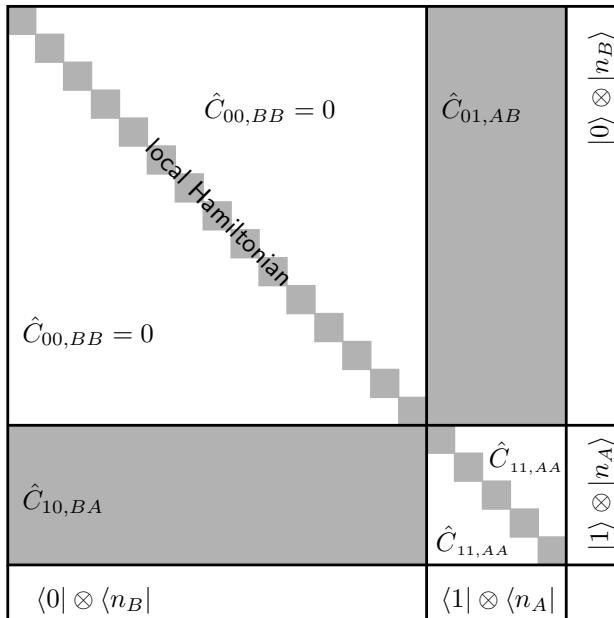


Figure 8.1.: Effective Hamiltonian model.

8.1.1. Effective Hamiltonian Model

In order to derive a closed dynamical equation for the density matrix elements it is inevitable to restrict the time evolution to a proper subspace of the complete Hilbert space of states. This subspace is chosen by the respective initial state. Here, we consider an evolution from an initial state, with the system in the excited state $|1\rangle$ and the environment somewhere in the lower band. Due to overall energy conservation the only other set of states that the full system can evolve into, is the set with the considered system in the ground state $|0\rangle$ and the environment in its upper band. Of course we may also start in a superposition of those states, referring to entangled¹ initial states – strong correlations between system and reservoir. However, the reduced model does not allow for initial states which contain correlations in the system, i.e. the off-diagonal element is zero at all times. This follows from the fact that we have skipped, e.g. the subspace where system and reservoir are in their ground state.

¹Note that correlated initial states are in principle also allowed for standard projection operator techniques, but they are very complicated to treat.

Implementing overall energy conservation in the reduced model, we skip all interaction terms which couple some other energy subspaces. Thus, as a canonical interaction part we keep $\hat{C}_{01,AB}$ only, referring to a transition between the above described energetically *allowed* states.

Furthermore, in order to consider thermalization only, we choose all microcanonical interaction parts to be zero, especially $\hat{C}_{00,BB} = \hat{C}_{11,AA} = 0$ (cf. Fig. 6.2). The complete effective Hamiltonian within this relevant subspace of the entire Hilbert space may thus be organized as shown in Fig. 8.1. The indices n_A (n_B) count the levels in the lower (upper) band with N_A respectively N_B states equally distributed over a band width of $\delta\epsilon$. The state density within the a th band is thus given by $N_a/\delta\epsilon$.

The quantity of interest in this context is of course the probability of finding the system S in its ground, respectively, excited state, thus, we investigate the diagonal elements of the reduced density operator. For the probability of finding the system excited we get

$$\rho_{11} = \sum_a P_{11,a} = P_{11,A} + P_{11,B}, \quad (8.1)$$

which follows from the reduced density matrix elements defined in (6.31). The second term is always zero ($P_{11,B} = 0$) since it belongs to another energy subspace which is not included in our present model and thus no initial state may populate such states where system and environment are excited as argued before.

To show that the integrated correlation function can indeed be linear in τ , we start again from (7.4) and not with the differential equation. Because of the special structure of the present interaction Hamiltonian most of the correlation functions in (7.4) vanish. This follows since almost all terms in the interaction operator are zero. Thus, the equation for the probability to find the system in its excited state simplifies to

$$P_{11,A}(t)(t + \tau) - P_{11,A}(t) = \frac{\text{Re}f_{10,AB}(\tau)}{\hbar^2} \left(\frac{P_{00,B}(t)}{N_B} - \frac{P_{11,A}(t)}{N_A} \right). \quad (8.2)$$

8.1.2. Correlation Function

In order to approach the HAM rate equation for the reduced model at hand, it remains to analyze the real part of the environmental correlation function. The correlation function is defined according to

$$g(\tau'') = \text{Tr}_E \{ \hat{C}_{01}(\tau'') \hat{\Pi}_B \hat{C}_{10} \hat{\Pi}_A \}. \quad (8.3)$$

The integrated correlation function (cf. (6.47)) thus reads

$$\text{Ref}_{10,AB}(\tau) = 2\text{Re} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' g(\tau'') . \quad (8.4)$$

Such a time ordered integral may be rewritten according to the transformation (cf. (A.15) and (A.18))

$$2\text{Re} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' g(\tau' - \tau'') = \int_0^\tau d\tau' \int_0^\tau d\tau'' g(\tau'' - \tau') . \quad (8.5)$$

Furthermore, using the transformation $\tau'' \rightarrow (\tau' - \tau'')$ the integrated environmental correlation function (8.4) yields

$$\text{Ref}_{10,AB}(\tau) = \int_0^\tau d\tau' \int_0^\tau d\tau'' \text{Tr}_E \{ \hat{C}_{01}(\tau') \hat{\Pi}_B \hat{C}_{10}(\tau'') \hat{\Pi}_A \} . \quad (8.6)$$

Plugging in the definition of the two environmental projection operators according to (6.1) and, furthermore, evaluating the partial trace over the environment, we get

$$\begin{aligned} \text{Ref}_{10,AB}(\tau) &= \int_0^\tau d\tau' \int_0^\tau d\tau'' \sum_{n_A} \sum_{n_B} \langle n_A | \hat{C}_{01}(\tau') | n_B \rangle \langle n_B | \hat{C}_{10}(\tau'') | n_A \rangle \\ &= \sum_{n_A} \sum_{n_B} \int_0^\tau d\tau' \langle n_A | \hat{C}_{01}(\tau') | n_B \rangle \int_0^\tau d\tau'' \langle n_B | \hat{C}_{10}(\tau'') | n_A \rangle \end{aligned} \quad (8.7)$$

Since $\hat{C}_{10} = \hat{C}_{01}^\dagger$, the second integration is exactly the complex conjugate of the first one and we may rewrite

$$\text{Ref}_{10,AB}(\tau) = \sum_{n_A} \sum_{n_B} \left| \int_0^\tau d\tau' \langle n_A | \hat{C}_{01}(\tau') | n_B \rangle \right|^2 . \quad (8.8)$$

The transition frequency from n_B to n_A is given by $\omega_{n_B n_A}$. The band width $\delta\epsilon$ is much smaller than the energy splitting between the bands $\Delta E \gg \delta\epsilon$. Furthermore, this energy splitting between bands is in resonance with the level spacing in the system. Thus, this band-band transition frequency is approximately $\omega_{n_B n_A} \approx \omega_{01}$. Using the definition of a time dependent operator in the interaction picture (6.20), we get

$$\begin{aligned} \text{Ref}_{10,AB}(\tau) &= \sum_{n_A} \sum_{n_B} \left| \int_0^\tau d\tau' e^{i\omega_{01}\tau'} \langle n_A | e^{i\hat{H}_E\tau'/\hbar} \hat{C}_{01} e^{-i\hat{H}_E\tau'/\hbar} | n_B \rangle \right|^2 \\ &= \sum_{n_A} \sum_{n_B} \left| \int_0^\tau d\tau' e^{-i(\omega_{n_A n_B} - \omega_{01})\tau'} \langle n_A | \hat{C}_{01} | n_B \rangle \right|^2 . \end{aligned} \quad (8.9)$$

Let us introduce a shorthand for the indices $u \equiv n_A$ and $v \equiv n_B$. By defining the frequency displacement

$$\omega_{uv} = \omega_{n_A n_B} - \omega_{01} \quad (8.10)$$

the integration yields

$$\text{Ref}_{10,AB}(\tau) = 4 \sum_{u,v} \frac{\sin^2(\omega_{uv}\tau/2)}{\omega_{uv}^2} |\langle u | \hat{C}_{01} | v \rangle|^2. \quad (8.11)$$

Obviously, this quantity is real and thus we get $\text{Ref}_{10,AB} = f_{10,AB}$. This is just the standard result as in derivations of Fermi's Golden Rule (see, e.g. [134]).

8.1.3. Linear Regime

Our arguments, including the conditions we have to impose on the model, are close to those brought forth in the context of Fermi's Golden Rule [40, 134]. The summation in (8.11) consists of two different terms: the transition probability or elements of the interaction matrix and a weight $f(\omega)$ ². The function

$$f(\omega) = \frac{\sin^2(\omega\tau/2)}{\omega^2} \quad (8.12)$$

has basically a peak at $\omega = \omega_{01}$ (see Fig. 8.2), with the width $\delta\omega = 4\pi/\tau$ and a height $f(\omega_{01}) = \tau^2/4$. The area under the function is $F = \pi\tau/2$.

As long as τ increases the peak gets higher and narrower. The height of the peak grows with the square of the time τ , the area under f only linearly with τ . At the very beginning, f is extremely broad and therefore much broader than the maximum frequency distance between two transitions, i.e. the maximal ω_{uv} . Since both bands are of the same width this maximal value is simply the band width $\delta\epsilon$ divided by \hbar . In this case we expect that (8.11) grows with the square of τ , because all terms are close to the maximum of the peak (see Fig. 8.3).

However, the behavior changes when the peak gets as broad as the frequency spectrum. We choose some τ_1 such that the width $\delta\omega(\tau_1)$ of $f(\omega)$ approximately has the same value as $\delta\epsilon/\hbar$

$$\delta\omega(\tau_1) = \frac{4\pi}{\tau_1} \approx \frac{\delta\epsilon}{\hbar} \Rightarrow \tau_1 = \frac{4\pi\hbar}{\delta\epsilon}. \quad (8.13)$$

²Here, we may think about a quasi continuous distribution of levels in the environmental band, thus ω_{uv} becomes a continuous variable.

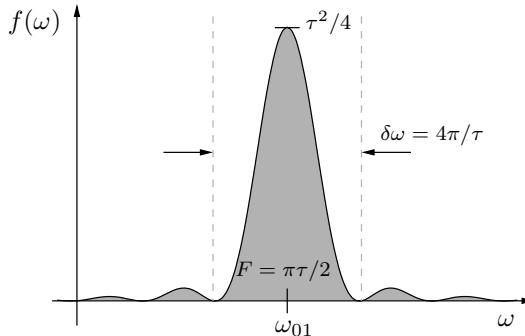


Figure 8.2.: The function $f(\omega)$ defined in (8.12).

Thus, the terms are distributed over the whole width of the peak and we expect that the sum grows proportional to the area under the peak, thus linearly in τ (see Fig. 8.3). One could thus expect two principally different behaviors: the square- and the linear regime.

Later at some time τ_2 , when the peak gets too narrow (see Fig. 8.3), i.e., the width gets smaller than the distance between two adjacent frequencies. The linear regime is left again. For the present model (see Fig. 6.1) the levels are equally distributed over the band. Thus, the splitting is given by $\delta\epsilon$ divided by the number N_B of levels in the band. The frequency between two adjacent levels in the band B reads

$$\Delta\omega = \frac{\delta\epsilon}{\hbar N_B} . \quad (8.14)$$

The time τ_2 is then given by

$$\delta\omega(\tau_2) = \frac{4\pi}{\tau_2} \approx \Delta\omega = \frac{\delta\epsilon}{\hbar N_B} \quad \Rightarrow \quad \tau_2 = \frac{4\pi\hbar N_B}{\delta\epsilon} . \quad (8.15)$$

Finally, for $\tau \rightarrow \infty$, f approaches a delta peak.

However, here we are mainly interested in the *linear regime* ($\tau_1 \leq \tau \leq \tau_2$), for which we guess that (8.11) grows linearly with τ . Here, the summation in (8.11) will average out the different elements of the interaction matrix if the function f does not change much over many summation steps. Thus, we replace the concrete interaction matrix element in (8.11) by the average matrix element

$$\left| \langle u | \hat{C}_{01} | v \rangle \right|^2 \approx \frac{1}{N_A N_B} \sum_{uv} \left| \langle u | \hat{C}_{01} | v \rangle \right|^2 = \lambda_{01,AB}^2 , \quad (8.16)$$

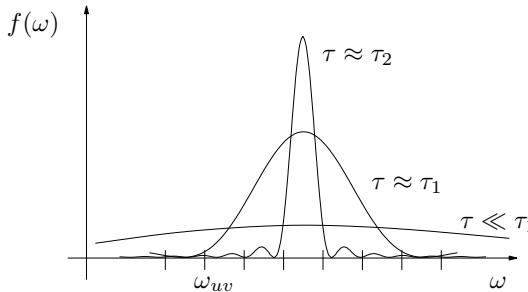


Figure 8.3.: Properties of the function $f(\omega)$ (cf. (8.12)) for different τ . Square and linear regime.

given by the coupling strength (6.12). Equation (8.11) thus reduces to

$$f_{10,AB}(\tau) \approx 4\lambda_{01,AB}^2 \sum_{uv} \frac{\sin^2(\omega_{uv}\tau/2)}{\omega_{uv}^2}. \quad (8.17)$$

Instead of summing over the energy levels in the final band B we switch to an integration in frequency space

$$\sum_v \rightarrow \int \frac{d\omega}{\Delta\omega}. \quad (8.18)$$

Thus, (8.17) yields

$$f_{10,AB}(\tau) \approx 4\lambda_{01,AB}^2 \sum_{u=1}^{N_A} \int \frac{\sin^2(\omega\tau/2)}{\omega^2} \frac{d\omega}{\Delta\omega}. \quad (8.19)$$

The integration is given by the area under the function f . Plugging in the respective area and summing over all initial states in band A we finally get

$$f_{10,AB}(\tau) \approx 4\lambda_{01,AB}^2 \sum_{u=1}^{N_A} \frac{F}{\Delta\omega} = \frac{2\pi\hbar\lambda_{01,AB}^2 N_A N_B}{\delta\epsilon} \tau. \quad (8.20)$$

The whole approximation is valid only if the width of the peak at the starting time of the linear regime τ_1 is much bigger than the level spacing in frequency space, i.e., if

$$\Delta\omega = \frac{\delta\epsilon}{N_B \hbar} \ll \delta\omega(\tau_1) = \frac{\delta\epsilon}{\hbar} \Rightarrow N_B \gg 1 \quad (8.21)$$

which is indeed the case for a suitable chosen environment, with many levels in the upper band B .

8.2. The HAM Rate Equation

Inserting the approximation (8.20) of the integrated correlation function (8.11) into (8.2) yields

$$P_{11,A}(t + \tau) = P_{11,A}(t) + \frac{2\pi\lambda^2 N_A N_B \tau}{\delta\epsilon\hbar} \left(\frac{P_{00,B}(t)}{N_B} - \frac{P_{11,A}(t)}{N_A} \right), \quad (8.22)$$

where we have abbreviated the coupling strength $\lambda_{01,AB} = \lambda$. The respective equation for the probability $P_{00,B}$ the second diagonal element of the reduced density operator can be obtained by exchanging indices. Equation (8.22) describes, within the discussed limits, a short time step starting from any allowed initial state. Since this formula is directly connecting the probabilities $P_{11,A}(t)$ of the initial state with those of the state reached after time τ , we can now iterate this equation under some specific conditions.

Before iterating the above equation (8.22), one should again check the pre-conditions for the short time step equation derived so far. We have only considered terms up to second order, and we can only iterate after a time step of length τ_1 . Thus, we have to make sure that the considered second order terms are still small compared to one after τ_1 , to justify the dropping of higher order terms. Furthermore, we should make sure that we iterate before the linear regime is left again, i.e. before τ_2 . Therefore we must additionally consider the second order terms at τ_2 compared to one. From these limits (cf. [40]) we finally get some criteria³ for the applicability of the approximations and therefore for the whole theory

$$\frac{\lambda}{\delta\epsilon} N_B \geq \frac{1}{2}, \quad \frac{\lambda^2}{\delta\epsilon^2} N_B \ll 1. \quad (8.23)$$

Meeting those conditions we can iterate (8.22). In the limit of τ being extremely small and replacing $P_{11,A}(t)$ by $\rho_{11}(t)$ and $P_{00,B}(t)$ by $\rho_{00}(t)$ as follows from (8.1) we find

$$\frac{d}{dt} \rho_{11}(t) = \frac{2\pi\lambda^2}{\delta\epsilon\hbar} (N_A \rho_{00}(t) - N_B \rho_{11}(t)), \quad (8.24)$$

$$\frac{d}{dt} \rho_{00}(t) = \frac{2\pi\lambda^2}{\delta\epsilon\hbar} (N_B \rho_{11}(t) - N_A \rho_{00}(t)). \quad (8.25)$$

The second dynamical equation for the change of the probability of finding the system in its ground state is obtained by just exchanging the indices.

³In honour of Peter Borowski who first implemented such finite bath models numerically those criteria are sometimes called Peter-criteria.

This evolution equation for the probabilities obviously conserves the overall probability. We have obtained a *rate equation* for the probabilities to find the system in the upper respectively lower level, which has as a solution just an exponential decay to an equilibrium state with a distribution according to the spectrum of the environmental system. That such a behavior indeed emerges from pure Schrödinger dynamics of a respective system class will be shown in the next Section by considering a special model class.

Comparing the above rate equation with the damped Bloch equations [97] in Lindblad form

$$\frac{d}{dt}\rho_{11}(t) = W_{10}\rho_{00}(t) - W_{01}\rho_{11}(t), \quad (8.26)$$

$$\frac{d}{dt}\rho_{00}(t) = W_{01}\rho_{11}(t) - W_{10}\rho_{00}(t), \quad (8.27)$$

we may identify the rates W_{ij} by

$$W_{10} = \frac{2\pi}{\hbar} \lambda_0^2 \frac{N_A}{\delta\epsilon}, \quad W_{01} = \frac{2\pi}{\hbar} \lambda_0^2 \frac{N_B}{\delta\epsilon}. \quad (8.28)$$

Thus, we find the rates being proportional to the square of the coupling strength times the state density of the respective band $N_{A/B}/\delta\epsilon$. This special density is called spectral density within the theory of Caldeira and Leggett.

Defining the decay time

$$T_{\text{th}} = \frac{1}{W_{10} + W_{01}}, \quad (8.29)$$

the solution of such a rate equation in case we start in the excited state of the system and in the lower band of the environment reads

$$\rho_{11}(t) = \frac{1}{W_{10} + W_{01}} (W_{01}e^{-t/T_{\text{th}}} + W_{10}), \quad (8.30)$$

$$\rho_{00}(t) = \frac{W_{01}}{W_{10} + W_{01}} (1 - e^{-t/T_{\text{th}}}). \quad (8.31)$$

Thus, as expected the solution describes an exponential decay into a final stationary state.

8.3. Comparison to Schrödinger Dynamics

To show that it is indeed possible to get a purely statistical behavior from a time-reversible Schrödinger equation we will compare the above theoretical

investigations to a complete solution of the Schrödinger equation in the following. Of course a statistical behavior is only feasible if the model is chosen in such a way that the respective conditions are met. But, nevertheless, it seems amazing that such a statistical behavior from a time-reversible equation could be feasible at all. Furthermore, inspite of the fact that the environment is large compared to the system itself, it is far away from being infinite. Thus, such a decay behavior could be observed even in a very small system, e.g. a spin coupled to only one single molecule. From a classical point of view this is definitely not possible since all thermodynamical properties appear for large systems and many particles only.

The presented theory could be used to investigate larger quantum mechanical systems without computing its whole time-evolution according to the Schrödinger equation which is not possible in most cases. Furthermore, the method is also able to handle some situations in which other methods definitely fail, e.g. entangled initial states between system and bath.

For all numerical investigations we use complex Gaussian distributed random matrices with zero mean to model a very general coupling without any peculiarities (see [112]). The Gaussian matrices will be normalized according to the definition of the coupling strength (6.12), such that the overall interaction strength can be adjusted by just a parameter λ . The normalized Gaussian matrix times the coupling strength is then used as a proper interaction matrix block in the Hamiltonian (see Fig. 8.1). For matrices from this kind the mentioned special conditions (see Sect. 6.1) apply: Only adjoint blocks are correlated and the traces (6.15) and (6.16) are extremely small for Gaussian random numbers with zero mean. Of course, in the present reduced model all of those special conditions are trivially fulfilled, since we chose all those blocks to be zero at the beginning. This interaction type has been chosen in order to keep the model as general and free from peculiarities as possible. For example, in the fields of nuclear physics or quantum chaos random matrices are routinely used to model unknown interaction potentials. However, we analyze the dynamics generated by one single interaction, not the average dynamics of a Gaussian ensemble of interaction matrices.

8.3.1. Finite Environment Imposing Infinite Temperature

First, we investigate the model depicted in Fig. 6.1 with the same amount of levels in the upper and lower band $N_A = N_B = 500$. The splitting⁴ of the two level system is $\Delta E = 25$ whereas the band widths are small with $\delta\epsilon = 0.5$. System and environment are coupled by a random interaction of strength

⁴Note that all energies are measured according to an arbitrary energy unit.

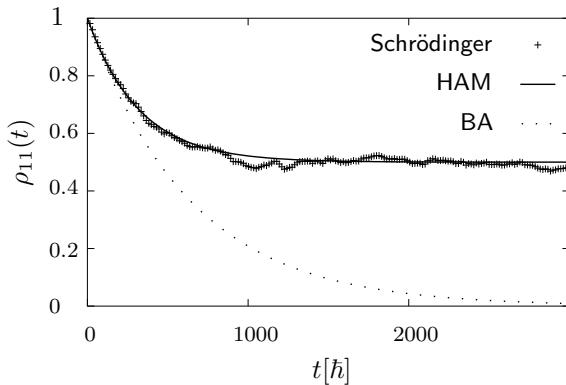


Figure 8.4.: Evolution of the excitation probability ($N_A = N_B = 500$).

$\lambda = 5 \times 10^{-4}$, according to its definition in (8.16). Initially starting in the excited level of the system and the lower band of the environment the Hilbert space average method leads to the above rate equation. Thus, in Fig. 8.4 we compare the result of the solution of the exact Schrödinger equation for the complete system (system and environment Schrödinger dynamics) to the rate equation and its solution (8.30) and (8.31). Furthermore, we include the standard result of a master equation derived in Born approximation (BA) as done, e.g. in [12], showing a wrong final equilibrium state (dotted line in Fig. 8.4, cf. Sect. 5.2).

Although the model is Markovian in the sense that bath correlations decay much faster than the system relaxes and its relaxation appears locally statistical, i.e. a closed equation for the density matrix elements of the system is feasible, the excitation probability of S significantly deviates from what the BA predicts: The beginning is correctly described, but rather than ending up at the temperature of the environment $T = T_E = 0$ as the BA predicts for thermal states in the environment [13], S ends up at $T = \infty$, i.e. equal occupation probabilities for both levels. Furthermore, a condition often attributed to the BA, namely that S and E remain unentangled⁵, is not fulfilled: When S has reached equilibrium the full system is in a superposition of S being excited, E in the lower band and S in the ground state, E in the upper band. This is

⁵In a private conversation Breuer pointed out that the system reservoir factorization approximation at any time is not necessary for standard projection operator techniques. However, it is often used since the derivation of the master equation is then much easier (see e.g. [97, p. 245]). But, that does not mean that system and bath must necessarily remain unentangled at any time.

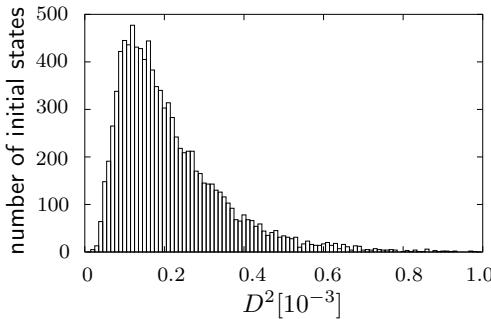


Figure 8.5.: Deviation of the exact evolution of the spins excitation probability from the HAM prediction for a set of entangled initial states.

a maximum entangled state with two orthogonal addends, one of which features a bath population corresponding to $T_E \approx 0$, the other a bath population inversion, i.e. even a negative bath temperature. These findings contradict the concept of factorizability, but are in accord with a result from [40] claiming that an evolution towards local equilibrium is always accompanied by an increase of system-bath correlations.

8.3.2. Accuracy of HAM

Since HAM is just a “best guess theory” the exact evolution follows its predictions with different accuracies for different initial states, even if all conditions on the model are fulfilled. To analyze this for, say $\rho_{11}(t)$, we introduce D^2 , as the time-averaged quadratic deviation of HAM from the exact (Schrödinger) result

$$D^2 = \frac{1}{\nu T_{\text{th}}} \int_0^{\nu T_{\text{th}}} dt \left(\rho_{11}^{\text{HAM}}(t) - \rho_{11}^{\text{exact}}(t) \right)^2. \quad (8.32)$$

Thus, D is a measure of the deviations from the predicted behavior. The results of the investigation for our model (see Fig. 6.1) are condensed into the histogram (Fig. 8.5, $\nu = 3$, $N_A = N_B = N = 500$). The set of respective initial states is characterized by a probability of $3/4$ for S in its excited state, E in its lower band and $1/4$ for S in its ground state, E in its upper band. Within these restrictions the initial states are uniformly distributed in the corresponding Hilbert subspace. Since all of them are correlated the application of a product projection operator technique would practically be unfeasible. However, as Fig. 8.5 shows, the vast majority of them follows the HAM prediction quite closely, although there is a typical fluctuation due to the finite size of the

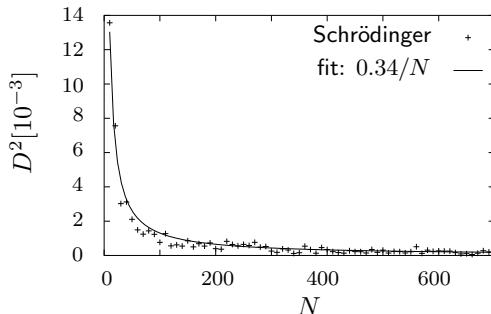


Figure 8.6.: Deviation of the exact evolution of the spins excitation probability from the HAM prediction for increasing number N of states per band in the environment.

environment of $D = \sqrt{2} \cdot 10^{-2}$ which is small compared to the features of the predicted behavior (which are on the order of one).

In Fig. 8.6 the dependence of D^2 on the number of states of E is displayed for $N_A = N_B = N = 10, \dots, 800$ (one evolution for each environment size). At $N = 500$ like used in the above accuracy investigation we find the same typical fluctuation, whereas for smaller environments the typical deviation is much bigger. We find that the squared deviation scales as $1/N$ with the environmental size, thus making HAM a reasonably reliable guess for many-state environments.

9. Decoherence

Most generally, decoherence typically comes about when the variables describing the entire system of interest naturally separate into “slow” and “fast” whether or not this separation corresponds to, respectively, system and environment.

J. J. Halliwell in [51]

In the last Chapter we have presented a reduced model system containing an energy exchanging contact between system and reservoir only. This contact has led to thermalization, i.e. decay of diagonal elements in the system density operator. However, the respective reduced model does not allow for the investigation of decoherence (cf. Sect. 8.1). As discussed in the last Chapter, we have explicitly excluded all states with correlations¹ inside the system of interest so far. Thus, we could never get any finite off-diagonal element in the reduced density operator of the system.

By including those internal correlated states in our reduced model we could have observed decoherence, too (see [39]). But, in such a model situation, decoherence is only induced by the energy exchanging system bath interaction, since we furthermore skipped all other interaction parts. Thus, in such models the respective decoherence time would be strictly bound to the thermalization time of the system.

We therefore go on to investigate an advanced model here. Besides the thermalizing blocks in the interaction there are possibly some microcanonical terms leading to decoherence. Restricting ourselves to parts of the microcanonical interaction which do not contribute to the energy exchange between system and reservoir (cf. Sect. 6.1 and especially Fig. 6.2), the thermalization time keeps unchanged. However, those extra blocks would definitely change the decoherence time.

Besides the theoretical investigation of the advanced model, we will also compare those results following from the HAM to the exact solution of the full Schrödinger equation of system and reservoir together.

¹Note that in contrast to the correlations in the last Chapter, referring to entanglement between system and reservoir, we address here correlations inside the system only.

9.1. Fermi's Golden Rule

So far, we have derived the most general form of the rate equations in Sect. 7.2, yielding (cf. (7.12) and (7.13))

$$\frac{d}{dt}P_{ii,a}(t) = \frac{1}{\hbar^2} \sum_{mb} \gamma_{im,ab} \left(P_{mm,b}(t) - \frac{N_b}{N_a} P_{ii,a}(t) \right), \quad (9.1)$$

$$\frac{d}{dt}|P_{ij,a}(t)|^2 = -\frac{1}{\hbar^2} |P_{ij,a}(t)|^2 \sum_{mb} (\gamma_{mi,ba} + \gamma_{mj,ba}). \quad (9.2)$$

There are mainly two possibilities of getting the concrete value of those rates $\gamma_{im,ab}$: Firstly, one could directly integrate the environmental correlation function by plugging in the respective system reservoir interaction into (6.47). Secondly, those rates may be approximated as presented in the last Chapter. But, typically, $\gamma_{im,ab}$ corresponds to a transition rate as obtained from Fermi's Golden Rule² and is, thus, simply chosen according to the celebrated statement. Following this last proposition the rate for a transition is proportional to the density of final states and the square of the transition matrix element, i.e. the coupling strength (6.12) of the system-environment interaction

$$\gamma_{im,ab} \approx 2\pi\hbar\lambda_{im,ab}^2 \frac{N_a}{\delta\epsilon}, \quad (9.3)$$

where $\delta\epsilon$ is the band width of the final band a ($N_a/\delta\epsilon$ state density). Using this approximation in (9.1) and (9.2) one gets

$$\frac{d}{dt}P_{ii,a}(t) = \frac{2\pi}{\hbar\delta\epsilon} \sum_{mb} \lambda_{im,ab}^2 (N_a P_{mm,b}(t) - N_b P_{ii,a}(t)), \quad (9.4)$$

$$\frac{d}{dt}|P_{ij,a}(t)|^2 = -\frac{2\pi}{\hbar\delta\epsilon} |P_{ij,a}(t)|^2 \sum_{mb} N_b (\lambda_{mi,ba}^2 + \lambda_{mj,ba}^2). \quad (9.5)$$

The resonance property, i.e. only energy conserving rates are nonzero in good approximation (remember $E_i - E_m \approx E_a - E_b$), is taken over by the coupling strengths $\lambda_{im,ab}$ here.

9.2. Advanced Model System

As already discussed the simplest model allowing for a closed dynamical equation on the basis of the elements of the density matrix of the system, is not

²For more details of the application of Fermi's Golden Rule in HAM scenarios see Chap. 8 or [38, 40].

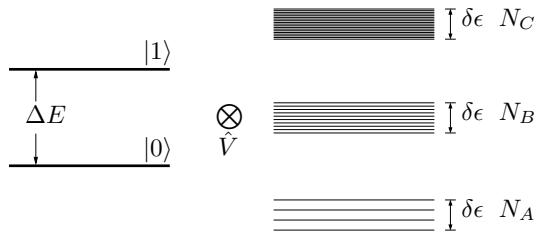


Figure 9.1.: Three band model for the investigation of the decay to equilibrium with finite temperature and the off-diagonal decay.

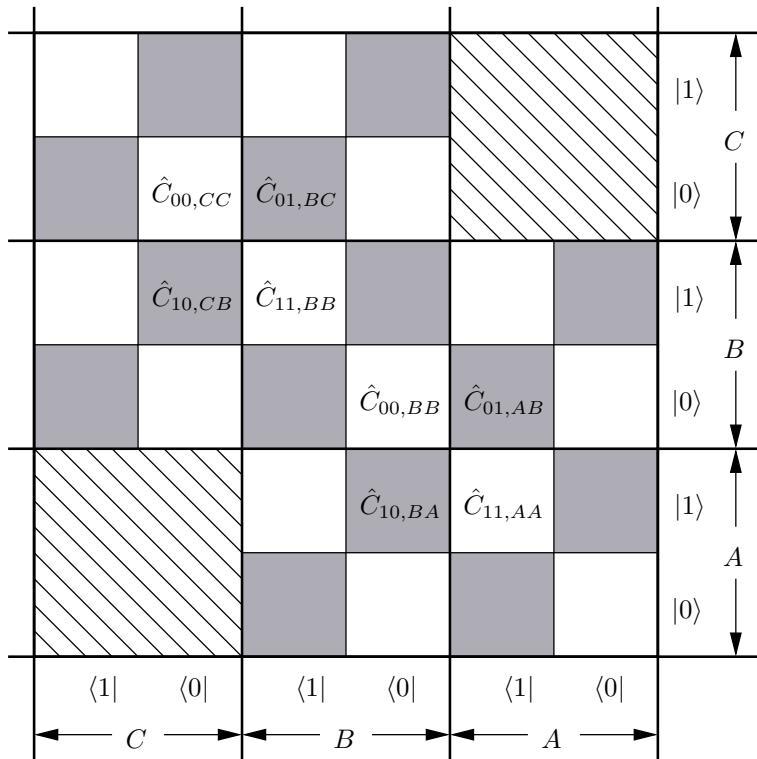


Figure 9.2.: Interaction matrix between system and environment for the model Fig. 9.1, canonical blocks (gray), microcanonical blocks (white), energetically forbidden blocks for weak couplings (hatched block).

suitable for the investigation of any off-diagonal decay. We thus introduce another simple model system depicted in Fig. 9.1. Again the system of interest just contains two energy levels. However, the environment consists of three bands of the same width and, eventually, a different number of levels per band.

The complete interaction Hamiltonian is shown in Fig. 9.2. For all numerical investigations we again choose the coupling matrices to be independent and identically distributed complex Gaussian random matrices. Thus, the interaction satisfies the additional criteria Sect. 6.1. We neglect all blocks referring to transitions which are energetically extremely unprobable, e.g. a transition from band A to band C (hatched part in Fig. 9.2), irrespective of what is going on in the system meanwhile. Furthermore, we skip all parts of the interaction inducing transitions in the system or the reservoir, but doing nothing in the respective other part, as done already in the last Chapter.

Finally we restrict ourselves to a special set of initial states: For the system we choose a superposition of both energy levels, whereas the reservoir is to be found in the middle band B . Thus, the respective set of states reads

$$|\psi(0)\rangle = (\varphi_0|0\rangle + \varphi_1|1\rangle) \otimes |\text{any state in the middle band}\rangle, \quad (9.6)$$

with $|\varphi_0|^2 + |\varphi_1|^2 = 1$. Obviously, those states are separable states of system and reservoir. The initial density matrix of the system is given by

$$\rho_{00} = |\varphi_0|^2, \quad \rho_{11} = |\varphi_1|^2, \quad \rho_{01} = \rho_{10}^* = \varphi_0\varphi_1^*, \quad (9.7)$$

which could contain an off-diagonal contribution. Thus, initially starting with probability $P_{00,B}$ and $P_{11,B}$ only, the respective other set of reachable states refers to the system in the ground state and the reservoir in C ($P_{00,C}$), as well as the system excited and the reservoir in A ($P_{11,A}$), due to overall energy conservation. Using (6.31) the density matrix elements of the system read

$$\rho_{11} = P_{11,A} + P_{11,B}, \quad \rho_{00} = P_{00,B} + P_{00,C}. \quad (9.8)$$

Again, we find the remaining two subspaces never to be occupied, i.e. $P_{00,A} = P_{11,C} = 0$.

Finally, taking all of those restrictions into account only the canonical interaction blocks $\hat{C}_{01,AB}$ and $\hat{C}_{01,BC}$ as well as their respective adjoints and the microcanonical blocks $\hat{C}_{11,AA}$, $\hat{C}_{00,BB}$, $\hat{C}_{11,BB}$ and $\hat{C}_{00,CC}$ are nonzero (cf. Fig. 9.2). Moreover, we choose the same coupling strengths within the canonical blocks, λ_{can} , as well as within the microcanonical ones, λ_{mic} .

9.3. Several Different Thermalization Times

We first concentrate on the thermalization within the advanced model system introduced in the last Section. Plugging in the model details into (9.4) we get the set of differential equations, one for each subspace probability separately

$$\frac{dP_{11,A}}{dt} = \frac{2\pi\lambda_{\text{can}}^2}{\hbar\delta\epsilon}(N_A P_{00,B} - N_B P_{11,A}), \quad (9.9)$$

$$\frac{dP_{11,B}}{dt} = \frac{2\pi\lambda_{\text{can}}^2}{\hbar\delta\epsilon}(N_B P_{00,C} - N_C P_{11,B}), \quad (9.10)$$

$$\frac{dP_{00,B}}{dt} = \frac{2\pi\lambda_{\text{can}}^2}{\hbar\delta\epsilon}(N_B P_{11,A} - N_A P_{00,B}), \quad (9.11)$$

$$\frac{dP_{00,C}}{dt} = \frac{2\pi\lambda_{\text{can}}^2}{\hbar\delta\epsilon}(N_C P_{11,B} - N_B P_{00,C}). \quad (9.12)$$

Unfortunately, it is not possible to combine those equations according to (9.8) in such a way that they only depend on ρ_{00} and ρ_{11} . Especially on the right hand side of the respective equation, it is not possible to properly arrange the probabilities to obtain density matrix elements.

According to the special structure of (9.4) and the special selection of microcanonical interaction parts the decay of diagonal elements is not perturbed by the additional coupling terms. Defining a decay time for the lower, respectively upper subspace as

$$T_l = \frac{\hbar\delta\epsilon}{2\pi\lambda_{\text{can}}^2(N_A + N_B)}, \quad T_u = \frac{\hbar\delta\epsilon}{2\pi\lambda_{\text{can}}^2(N_B + N_C)}, \quad (9.13)$$

one finds the general solution of the set of differential equations together with the initial state (9.7)

$$P_{11,A} = |\varphi_0|^2 \frac{N_A}{N_A + N_B} (1 - e^{-t/T_l}), \quad (9.14)$$

$$P_{11,B} = |\varphi_1|^2 \frac{1}{N_B + N_C} (N_B + N_C e^{-t/T_u}), \quad (9.15)$$

$$P_{00,B} = |\varphi_0|^2 \frac{1}{N_A + N_B} (N_B + N_A e^{-t/T_l}), \quad (9.16)$$

$$P_{00,C} = |\varphi_1|^2 \frac{N_C}{N_B + N_C} (1 - e^{-t/T_u}). \quad (9.17)$$

Combining those solutions according to (9.8), we get functions for the diagonal elements of the reduced density matrix. However, note that those equations will show a decay according to two different decay times T_l and T_u in general.

In the following, let the number of levels in the environment increase exponentially with energy, i.e. we choose $N_A = N$, $N_B = 2N$ and $N_C = 4N$. This refers to a typical canonical environment³ within quantum thermodynamics (cf. [40]). An environment featuring such a level structure is associated with a spectral temperature⁴ $\beta = \ln 2$.

The final equilibrium state of the two-level system is only determined by the number of levels in the environment. Thus, starting with one of the above discussed initial states (9.6), the system decays to the same state with temperature $\beta = \ln 2$, irrespective of which concrete state is chosen. This finding is one of the central results of equilibrium quantum thermodynamics. For the probability of finding the system excited we get for $t \rightarrow \infty$

$$\begin{aligned}\rho_{11}(\infty) &= P_{11,A}(\infty) + P_{11,B}(\infty) \\ &= |\varphi_0|^2 \frac{N_A}{N_A + N_B} + |\varphi_1|^2 \frac{N_B}{N_B + N_C} = \frac{1}{3}\end{aligned}\quad (9.18)$$

where we have used the exponential increase of levels in the environment. Analogously, we find $\rho_{00}(\infty) = 2/3$ and $\rho_{01}(\infty) = 0$ (see [9, 10, 40]). According to (4.28), this refers to a state with finite temperature

$$\beta = \ln \frac{\rho_{00}(\infty)}{\rho_{11}(\infty)} = \ln 2. \quad (9.19)$$

The question remains, though, which route to equilibrium the system will choose.

In the following we would like to show that such a decay according to two different times is indeed feasible. The coupling between system and environment is again assumed to be a random Hermitian matrix, to avoid any bias, with coupling strength $\lambda_{\text{can}} = 5 \times 10^{-4}$. For the environment we choose an exponential increase of levels, i.e. $N_A = 200$, $N_B = 400$ and $N_C = 800$ in the respective band of width $\delta\epsilon = 0.5$. According to those model parameters and (9.13) we find for the two thermalization times, $T_l = 530.52$ and $T_u = 265.26$, respectively.

For the given model system it is possible to compute the criteria (8.23) for the applicability of the Hilbert space average method in the upper respectively lower subspace separately. However, we get different values for the upper and

³Modular constructed multilevel systems typically feature an exponential increase of energy levels with energy, see [40].

⁴Within quantum thermodynamics a temperature is enforced on the system according to the environmental level structure. The spectral temperature is thus defined for a spectrum enforcing the respective temperature (cf. [40]).

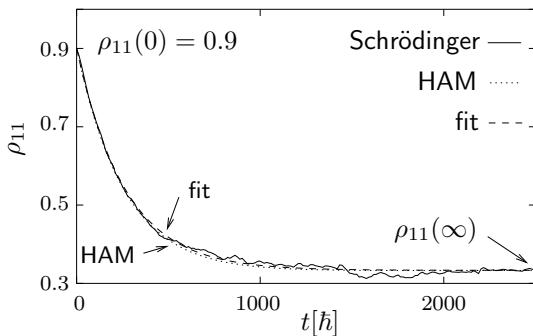


Figure 9.3.: Two time exponential decay: dotted line refers to HAM, dashed one to a single exponential fit, solid line is the exact Schrödinger solution.

lower part of the environment, finding

$$\text{lower subspace: } \lambda_{\text{can}} N_A / \delta\epsilon = 0.4, \quad \lambda_{\text{can}}^2 N_A / \delta\epsilon^2 = 0.0004, \quad (9.20)$$

$$\text{upper subspace: } \lambda_{\text{can}} N_B / \delta\epsilon = 0.8, \quad \lambda_{\text{can}}^2 N_B / \delta\epsilon^2 = 0.0008. \quad (9.21)$$

Since those values fulfill the respective conditions (8.23), HAM is applicable in each subspace. Thus, we expect a statistical behavior for the complete model.

For the special initial state we choose $\varphi_0 = 1/\sqrt{10}$ and $\varphi_1 = 3/\sqrt{10}$, corresponding to an initial probability in the excited state $\rho_{11}(0) = 0.9$. The result of the full solution of the Schrödinger equation for the respective model as well as the solution of the rate equation is depicted in Fig. 9.3. Additionally, we fit the data by a simple exponential function, finding a decay time in between the two times T_u and T_l . Obviously, the rate equation is again in very good accordance with the complete Schrödinger dynamics except for some finite size fluctuations.

To give an impression of a more complicated behavior we also investigate another initial state $\rho_{11}(0) = 0.5$ (see Fig. 9.4). Again, one finds a very good accordance between Schrödinger dynamics and theory, but a simple exponential fit completely fails here. In the example at hand one gets a decay according to two different decay times in a two-level system, which could never emerge from a standard quantum master equation.

By numerically solving the time dependent Schrödinger equation for the pure state of the full model we find for the reduced state of the system an exponential decay up to some fluctuations. For the baths initial state being a real mixed state one can even expect fluctuations to be smaller, since fluctuations corresponding to various pure addends of the mixed state should partially cancel each other. Thus, again, the Schrödingerian dynamics yields a

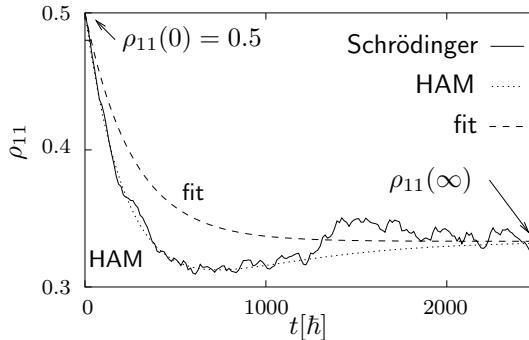


Figure 9.4.: Two time exponential decay as in Fig. 9.3, but for another initial state: HAM and the exact Schrödinger solution are in good accordance (two decay times). The exponential fit fails completely.

local behavior that is well described by the above developed theory, controlled by some transition rates.

9.4. Decoherence According to Canonical Couplings

The initial state (9.7) contains an off-diagonal element $\rho_{01} = \varphi_0 \varphi_1^*$. In the following we consider the time evolution of such an initial off-diagonal element in a system with only canonical couplings. Thus, we again choose all diagonal blocks, i.e. microcanonical couplings, in the interaction to be $\hat{C}_{00,CC} = \hat{C}_{11,BB} = \hat{C}_{00,BB} = \hat{C}_{11,AA} = 0$. According to (6.31), the off-diagonal element reads

$$\rho_{01} = P_{01,A} + P_{01,B} + P_{01,C} = P_{01,B}. \quad (9.22)$$

This follows from the fact that initially there was a nonzero probability in the middle band $P_{01,B}$ only, and since we skipped all interaction terms causing transitions to the other set of states, those other terms remain zero. Thus the absolute value of the off-diagonal element is just defined by $|P_{01,B}|^2$. Following (9.5) we get the dynamical equation

$$\frac{d}{dt} |P_{01,B}|^2 = -\frac{2\pi\lambda_{\text{can}}^2(N_A + N_C)}{\hbar\delta\epsilon} |P_{01,B}|^2 \quad (9.23)$$

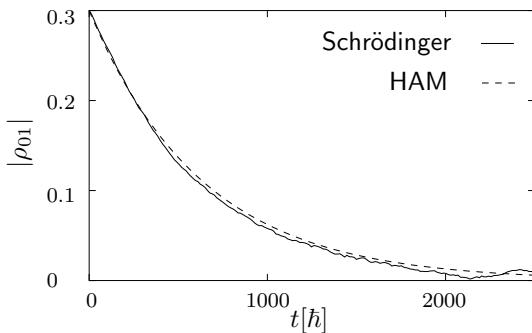


Figure 9.5.: Exponential decay of the off-diagonal element: HAM and the exact Schrödinger solution are in good accordance ($N_A = 200$, $N_B = 400$, $N_C = 800$, $\delta\epsilon = 0.5$, $\lambda_{\text{can}} = 5 \cdot 10^{-4}$, $T_{\text{dec}} = 636.6$).

where we used all the properties of the special model. We define the off-diagonal decay time (decoherence time)

$$T_{\text{dec}} = \frac{\hbar\delta\epsilon}{\pi\lambda_{\text{can}}^2(N_A + N_C)} \quad (9.24)$$

and get the general solution

$$|\rho_{01}(t)|^2 = |P_{01,B}(t)|^2 = |\varphi_0\varphi_1^*|^2 e^{-2t/T_{\text{dec}}} \quad (9.25)$$

Thus, the absolute value of the off-diagonal element reads

$$|\rho_{01}(t)| = |\varphi_0\varphi_1^*|e^{-t/T_{\text{dec}}} \quad (9.26)$$

In Fig. 9.5 we show (9.26) in comparison to the same value extracted from the complete integration of the Schrödinger equation. The model is the same as in the last Chapter yielding $T_{\text{dec}} = 636.6$. The investigation shows that one can indeed find an exponential decay of off-diagonal elements due to a canonical coupling with the environment.

9.5. Additional Microcanonical Coupling

The comparison of thermalization and decoherence time in the above models is ambiguous because of the strange two time behavior of the diagonal elements. We could eventually fit a simple exponential decay to the behavior of the first initial state in Fig. 9.3 using the resulting decay constant as a mean decay

time. However, for the second initial state Fig. 9.4 this seems to be more than questionable. The fit in Fig. 9.4 has nothing to do with the real dynamics.

Thus, let us again simplify the advanced model a little bit further. The new model should feature a single thermalization time to investigate the interesting connection of this time to the decay time of the off-diagonal element. The model is in principle the same as in Sect. 9.3 with the Hamiltonian Fig. 9.2. Here, we take all the discussed canonical as well as microcanonical couplings into account, but we choose the same number of levels in each band of the environment, i.e. $N_A = N_B = N_C = N$. Plugging this special model into the differential equations (9.9)-(9.12) it is possible to combine respectively two differential equations, finding a closed set of equations for the elements of the reduced density matrix. By using (9.8) we find

$$\frac{d\rho_{00}}{dt} = \frac{2\pi\lambda_{\text{can}}^2 N}{\hbar\delta\epsilon} (\rho_{11} - \rho_{00}), \quad (9.27)$$

$$\frac{d\rho_{11}}{dt} = \frac{2\pi\lambda_{\text{can}}^2 N}{\hbar\delta\epsilon} (\rho_{00} - \rho_{11}). \quad (9.28)$$

Thus we get, as in the investigation of the last Chapter (two band model), a simple dynamical equation, featuring an exponential decay according to the single time

$$T_{\text{th}} = \frac{\hbar\delta\epsilon}{4\pi\lambda_{\text{can}}^2 N}. \quad (9.29)$$

This decay time of diagonal elements is the same as previously defined in (8.29) for equally sized subspaces.

In comparison with Sect. 9.4, we get some more terms for the dynamical equation of the off-diagonal elements due to the additional microcanonical couplings. However, (9.22) remains to be valid. Using the structure of the interaction matrix one finds the differential equation

$$\frac{d}{dt} |P_{10,B}|^2 = -\frac{4\pi N}{\hbar\delta\epsilon} (\lambda_{01,AB}^2 + \lambda_{01,CB}^2 + \lambda_{11,BB}^2 + \lambda_{00,BB}^2 + \lambda_{10,AB}^2 + \lambda_{10,CB}^2) |P_{10,B}|^2, \quad (9.30)$$

where we have already skipped all non-energy conserving terms. Note that

$$\lambda_{01,AB}^2 = \lambda_{10,CB}^2 = \lambda_{\text{can}}^2, \quad (9.31)$$

$$\lambda_{11,BB}^2 = \lambda_{00,BB}^2 = \lambda_{\text{mic}}^2, \quad (9.32)$$

$$\lambda_{01,CB}^2 = \lambda_{10,AB}^2 = 0 \quad (9.33)$$

cf. Fig. 9.2. Thus, one gets

$$\frac{d}{dt} |P_{10,B}|^2 = -\frac{4\pi N(\lambda_{\text{can}}^2 + \lambda_{\text{mic}}^2)}{\hbar\delta\epsilon} |P_{10,B}|^2. \quad (9.34)$$

Using the definition $\xi = \lambda_{\text{mic}}/\lambda_{\text{can}}$, we find for the decoherence time

$$T_{\text{dec}} = \frac{\hbar\delta\epsilon}{2\pi N(\lambda_{\text{can}}^2 + \lambda_{\text{mic}}^2)} = \frac{\hbar\delta\epsilon}{2\pi N\lambda_{\text{can}}^2(1 + \xi^2)} = \frac{2T_{\text{th}}}{1 + \xi^2}. \quad (9.35)$$

According to this decoherence time and (9.22) we get a closed dynamical equation for the off-diagonal element, too

$$\frac{d}{dt} |\rho_{10}(t)|^2 = -\frac{2}{T_{\text{dec}}} |\rho_{10}(t)|^2. \quad (9.36)$$

Thus the solution decays according to

$$|\rho_{10}(t)| = |\varphi_0 \varphi_1^*| e^{-t/T_{\text{dec}}}. \quad (9.37)$$

For the absence of microcanonical coupling terms ($\lambda_{\text{mic}} = 0$) we immediately get the standard result $2T_{\text{th}} = T_{\text{dec}}$, a twice as fast thermalization compared to the decoherence. For finite λ_{mic} , T_{dec} gets shorter until we get $T_{\text{th}} = T_{\text{dec}}$ for $\lambda_{\text{mic}} = \lambda_{\text{can}}$. In case of $\lambda_{\text{mic}} \gg \lambda_{\text{can}}$ the decoherence is much faster than the relaxation as long as theory keeps applicable; all the above considerations require a small system environment coupling.

To show that it is indeed possible to get different time scales for the decay of diagonal elements of the density matrix (thermalization) and the decay of off-diagonal elements (decoherence) from pure Schrödinger dynamics, we will compare the above theoretical results with the exact full system dynamics using a system with $N = 500$, $\delta\epsilon = 0.5$, and $\lambda_{\text{can}} = 5 \cdot 10^{-4}$. The microcanonical interaction strength λ_{mic} is chosen in units of the canonical one, between $\xi = 0$ and $\xi = 5$ (cf. (9.35)). The initial state (9.7) contains nonzero off-diagonal elements, where we use again $\varphi_0 = 1/\sqrt{10}$ and $\varphi_1 = 3/\sqrt{10}$. Thus, we find $\rho_{10}(0) = 0.3$. A proper thermodynamical situation is characterized by a complete disappearance of correlations in equilibrium, referring to a maximum entropy state for the system (cf. [40]).

In Fig. 9.6 we present the off-diagonal decay time (9.35) of the system, according to the above theoretical considerations and a complete integration of the Schrödinger equation. By fitting an exponential function to the off-diagonal element decay from Schrödinger dynamics, we get the decoherence time T_{dec} in dependence of the microcanonical coupling strength. In Fig. 9.6 we show this numerical decoherence time T_{dec} over the microcanonical coupling strength, here over ξ .

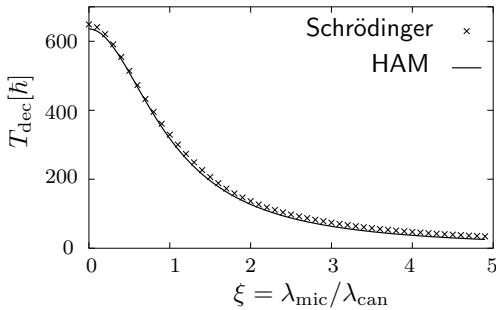


Figure 9.6.: Decoherence time over microcanonical interaction strength. HAM theory according to (9.35).

As can be seen, the numerical result is in very good accordance with our theory. Additionally we have checked the deviations from theory by using (8.32), comparing the decay of diagonal elements according to the full Schrödinger time evolution and HAM. Here, we find a small deviation, but less than $D = \sqrt{5} \cdot 10^{-2}$ (cf. typical deviations in Fig. 8.6). As argued before deviations increase for increasing microcanonical coupling strength. This limits the smallness of the decoherence time in comparison to the thermalization time, since for too strong microcanonical couplings the theory itself is not applicable any longer. Again, remember that all what is done above is only valid for a sufficient small system-environment coupling. Thus, for the small model system at hand it seems not feasible to get, say, a factor up to 10^{30} between thermalization and decoherence time, as stated in some standard text books (cf. [154]). But for reasonable large systems, featuring higher state densities, such a situation may come into reach.

Part II.

Transport

10. Heat Transport

No subject has more extensive relations with the progress of industry and the natural sciences; for the action of heat is always present, it penetrates all bodies and spaces, it influences the processes of the arts, and occurs in all phenomena of the universe.

J. Fourier in [33]

The complete last Part of this text has dealt with the old, but still interesting question, how a quantum system as a whole relaxes to a thermal equilibrium state due to the contact to another comparably large system – its environment. Besides some standard techniques like the quantum master equation we have also presented a quite new method, the Hilbert space average method, in order to investigate the decay in quantum mechanics. So far, we have not considered any further substructure within the system. However, in nature systems are typically constructed of identical subunits forming a topological structure in real space. If there is no global contact of the complete system to the environment any longer, but rather a local coupling to the reservoir at some edge of the system, a further important question immediately arises: How is energy or possibly heat transported through such a structure in real space? Again the question is quite old, but seems to attract more and more interest at the moment, since it is far from being completely answered, yet. The many different publications on the topic of *heat transport* indicates both an increasing interest in the problem and its nontrivial character, emphasized by the title of a recent publication “Fourier’s Law: A Challenge to Theorists” (see [8]).

This Chapter shall give a short introduction to the interesting phenomenon of transport of heat from the viewpoint of some different theoretical approaches. In such a nonequilibrium phenomenon as heat conduction, the intensive parameters of different parts of a system are no longer equal, i.e., there is no global equilibrium established inside the whole system. But, despite of this fact, in a *macroscopically small* but *microscopically large* part of the system one could nevertheless find something like an equilibrium state slightly

different from region to region (cf. [88]). Think, for example, of some material bar coupled at both ends to heat baths of different temperature. In this sort of experiment¹ one typically finds a constant temperature gradient within the material. Thus, there is no global temperature defined in the whole system, but in a small enough part one could approximately describe the system by a canonical equilibrium state with *local* temperature T .

The first theoretical as well as experimental investigation of heat transport through solids was done by Joseph Fourier about 1807 (see [33]). Therefore the first Section of the present Chapter is dedicated to his famous *Fourier's Law* according to which temperature or energy diffuse through the system. In the following we will sum up some of the main approaches to the famous law from a microscopic theory and several of their serious difficulties, before we give an overview of recent developments in the heat conduction research.

10.1. Fourier's Law

Almost two hundred years ago Fourier conjectured that temperature (or as we know today: energy) tends to diffuse through solids once close enough to equilibrium (cf. [33]). He considered the transport of heat on a phenomenological respectively macroscopic level, finding a partial differential equation for the heat transport through some material and trying to solve it by mathematical methods, e.g., the Fourier series expansion. Nowadays, Fourier is mainly known for his marvelous mathematical research, especially the celebrated Fourier analysis.

Considering a situation with a position and time dependent temperature profile within some material, Fourier describes the problem by an equation for the internal energy density $u(T(\mathbf{r}, t))$. The change of this quantity $u(T(\mathbf{r}, t))$ which is a function of the temperature T at position \mathbf{r} and time t should be proportional to the gradient of the thermodynamic force – here the temperature gradient

$$\frac{\partial}{\partial t} u(T(\mathbf{r}, t)) = \kappa \nabla \cdot \nabla T(\mathbf{r}, t), \quad (10.1)$$

with κ being the heat conductivity. As the energy density is a function of temperature one could also state that

$$\frac{\partial}{\partial t} u(T(\mathbf{r}, t)) = \frac{\partial u}{\partial T} \frac{\partial T}{\partial t} = \kappa \Delta T(\mathbf{r}, t), \quad (10.2)$$

¹"When heat is unequally distributed among the different parts of a solid mass, it tends to attain equilibrium, and passes slowly from the parts which are more heated to those which are less; and at the same time it is dissipated at the surface, and lost in the medium or in the void." (Fourier, [33, chap.1, p.15])

and by using the definition of the specific heat capacity

$$c(T) = \frac{\partial u}{\partial T} \quad (10.3)$$

one finds the *heat conduction equation*

$$\frac{\partial}{\partial t} T(\mathbf{r}, t) = \frac{\kappa}{c(T)} \Delta T(\mathbf{r}, t). \quad (10.4)$$

This diffusive behavior is slightly reformulated by applying the continuity equation for the energy density

$$\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{J} = 0, \quad (10.5)$$

where \mathbf{J} represents the heat current in the system. Plugging in (10.5) into (10.2) one finds

$$\nabla \cdot \mathbf{J} = -\nabla \cdot (\kappa \nabla T(\mathbf{r}, t)). \quad (10.6)$$

From these considerations one immediately gets what *Fourier's law* (1807) states close to thermal equilibrium: a proportionality between the heat current and the temperature gradient

$$\mathbf{J} = -\kappa \nabla T(\mathbf{r}, t). \quad (10.7)$$

Furthermore by thinking of the temperature T as being a function of the internal energy density u we can state for the energy current

$$\mathbf{J} = -\kappa \nabla T(u(\mathbf{r}, t)) = -\kappa \frac{\partial T}{\partial u} \nabla u = -\frac{\kappa}{c} \nabla u(\mathbf{r}, t), \quad (10.8)$$

where \mathbf{J} is now the energy current density.

Despite the ubiquitous nature of the phenomenon of heat conduction in our everyday experience, its explanation on the basis of some reversible microscopic dynamics remains a serious problem. The interesting quantity here is the material property κ – the heat conductivity. In the last two centuries there were several different microscopic approaches to Fourier's Law from a completely different background. The goal of all of those efforts was to give a thorough and comprehensive picture of heat transport from the viewpoint of a basic microscopic theory.

In the following Sections we will give a short overview of the central attempts and their main difficulties. Furthermore, we will try to summarize the recent developments from the viewpoint of classical mechanics or quantum mechanics as well as some new experimental investigations (see Sect. 10.5). Against this background, it would finally be very helpful to have a microscopic theory for heat transport for both experimental and even technical reasons.

10.2. Kinetic Gas Theory for Phonons

One of the first attempts to find a microscopic foundation for the heat conductivity of an insulating solid was due to Debye [22, 77]. He considered the phonons inside such a material as classical particles using results of the kinetic gas theory to describe the heat transport based on phonons.

Thinking of a particle current in one direction of a crystal, this current should be proportional to the density η of the particles and their mean velocity \bar{v} . A single phonon considered as a classical particle moving from a region with temperature $T + \Delta T$ to a region with temperature T loses the energy $C\Delta T$ with C being the heat capacity of the respective particle. According to the internal temperature gradient ∇T in between a free path \bar{l} of the phonon we find the temperature difference to be

$$\Delta T = \bar{l} \nabla T. \quad (10.9)$$

In such a situation the energy current is just proportional to the particle current times the transported energy and thus

$$\mathbf{J} \propto \eta \bar{v} C \Delta T \quad (10.10)$$

$$\propto \eta \bar{v} C \bar{l} \nabla T. \quad (10.11)$$

Reformulating this result by the heat capacity per volume $c = \eta C$ and comparing it to Fourier's Law (10.7) we find for the heat conductivity

$$\kappa \propto c \bar{v} \bar{l}. \quad (10.12)$$

Obviously, the free path of the phonons enters the above microscopic formula leading to an infinite heat conductivity² in case of no scattering processes in the solid. Why should phonons have a finite free path inside a material? Debye and his followers have mainly taken two processes into account which limit the free path of the phonons, the scattering at impurities (primarily in amorphous materials) and the phonon-phonon interaction in the solid (perfect crystal, lacking any impurities). However, if all lattice couplings are harmonic there is no scattering process between phonons and therefore there is no finite heat conductivity.

To describe the anharmonicity in the coupling of the atoms in the solid is a serious theoretical problem. Debye proposed that the Brownian motion of the atoms may produce an irregularity in the lattice³ and thereby a phonon source

² „Bei der vorhergehenden Rechnung wurde die freie Weglänge l eingeführt ...; $l = \infty$ bedeutet ... unendlich große Wärmeleitfähigkeit.“ (Debye, [22, p.50])

³ „...bei ihm [Kristall] sind bei tiefer Temperatur keine wesentlichen Unregelmäßigkeiten vorhanden. Aber man wird schon hier vermuten, daß eine Wärmebewegung solche Schwankungen sekundär erzeugen wird,...“ (Debye, [22, p.50])

for scattering in a perfect crystal. On this basis he was able to account for the mean free path of the phonons, finding it anti-proportional to the temperature of the solid. Finally he was able to compute an approximate formula for a finite heat conductivity (cf. [22]) from a microscopic point of view.

10.3. Peierls-Boltzmann Equation

A more detailed approach to the question of a microscopic foundation of Fourier's Law was suggested by Peierls in 1929 proposing a Boltzmann equation for the phonons in the solid [113–115]. Peierls mainly considered the anharmonicities in the atom coupling, which are the dominant effect of phonon scattering in pure crystals of not too small size and at not too low temperatures.

Using the anharmonic part of the interaction as a perturbation, Peierls was able to find conditions from Fermi's Golden Rule for the possible scattering processes: the energy conservation and the momentum conservation

$$\omega_1 + \omega_2 = \omega_3 , \quad (10.13)$$

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + n\mathbf{g} , \quad n \in \mathbb{Z} , \quad (10.14)$$

where (ω_1, \mathbf{k}_1) and (ω_2, \mathbf{k}_2) are the two incoming phonons (ω_3, \mathbf{k}_3) concerning the outgoing one and \mathbf{g} is the appropriate reciprocal lattice vector (cf. [77]). All processes with $\mathbf{g} = 0$ are not suitable for a thermalization of the phonon gas, since then the whole momentum of all phonons is conserved, the conductivity would again be infinite (all these processes are called *normal* or N-processes). Of vital importance for the existence of a thermal resistance are therefore the scattering processes with $\mathbf{g} \neq 0$ called *Umklappprozess*.

Considering now very low temperatures ($T < \Theta$, Θ Debye temperature) where most of the two incoming thermal activated phonons have not enough energy to fulfill the above scattering conditions, there is again no possible Umklapp-process. According to the Boltzmann distribution of phonon energies we expect that for low temperatures the number of high-energy phonons decreases by $e^{-\Theta/T}$. Cause of the vital importance of the Umklapp-process for a finite thermal resistance, the conductivity must be proportional to that exponential factor in the low temperature regime.

Since phonons are also scattered at impurities or boundaries of the crystal, one has to consider more scattering processes in order to find a comprehensive picture of heat conduction in solids (see e.g. [77, 99–101, 156]). These additional processes are very important for low temperatures, especially, since in this region the Umklapp-processes die out rapidly.

To describe the phonons inside the crystal Peierls essentially proposed a Boltzmann equation replacing classical gas particles by quantized quasiparticles, the phonons. Furthermore he assumed classical transition probabilities between different phonon modes obtained from Fermi's Golden Rule. This theory succeeds in explaining the basic transport properties of solids and allows to derive statements about the conductivity of insulating crystals. The equation itself is very hard to solve, but, nevertheless, one can obtain some tendencies in the temperature dependence of the conductivity⁴: finding a decrease for higher temperatures between $1/T$ and $1/T^2$.

In conclusion, the Peierls-Boltzmann theory faces conceptual shortcomings: quantized normal modes of a many particle system are described classically, i.e., being well localized in configuration as well as momentum space and showing no dispersion (cf. [115]). This becomes a serious problem at least in the limit of systems consisting of only a few particles at all. Already Debye's approach to heat conduction deals with a rather classical idea of the quasi-particles – thinking of bouncing balls like gas particles in a box instead of quantum mechanical objects. Furthermore, in order to exploit Fermi's Golden Rule, the actual quantum state of a phonon mode is discarded keeping only the mean occupation number. Due to the neglect of any phases, this is called the random phase approximation and replaces Boltzmann's Stosszahlansatz (see [115]). Strictly speaking these both lack justification though, and there are no clear criteria for the applicability of the theory. Additionally, the application⁵ of the theoretical concept to a concrete coupling model is very complicated and even today there are doubts about the importance of Umklapp-processes at all for a finite conductivity in solid states (see [30, 153]).

10.4. Linear Response Theory

Another powerful technique within the field of heat transport is the Green-Kubo formula. Derived on the basis of linear response theory it has originally been formulated for electrical transport [81, 82, 107]. The external force, e.g., the electric field is considered to be a perturbation of the system. In this context the current is viewed as the response to this external perturbative electrical potential which can be expressed as a part of the Hamiltonian of the system [81].

⁴“The only prediction that would seem to follow with certainty is that the law must be intermediate between T^{-1} and T^{-2} .” (Peierls, [115, p.51])

⁵“This seems a poor return for a long discussion, but progress beyond this stage is difficult, unless we could construct a dispersion law which was simple enough to allow us to list the solutions for the possible phonon collisions explicitly, and yet realistic enough to give the right kind of collision including those of the Umklapp type.” (Peierls, [115, p.52])

10.4.1. Currents, Forces and Onsager Relation

In a linear response theory, currents \mathbf{J}_i should be a linear function of external forces \mathbf{X}_j , defining the matrix of *response coefficients* Z_{ij} as

$$\mathbf{J}_i = \sum_j Z_{ij} \mathbf{X}_j . \quad (10.15)$$

From the Onsager relation we know that the coefficient matrix has to be symmetrical $Z_{ij} = Z_{ji}$ (see [21, 82, 96]).

The choice for the current operators and the corresponding forces is ambiguous. But it turns out that the Onsager relation is not valid for all choices. A special one for which the Onsager relation is valid was proposed by de Groot [21], who chose currents and forces in such a way that entropy increases

$$\frac{\partial S}{\partial t} = \sum_i \mathbf{J}_i \mathbf{X}_i > 0 , \quad (10.16)$$

since a nonequilibrium process should be combined with a net entropy production.

Considering a situation with two different fluxes, a particle current \mathbf{J}_1 due to an external force $\mathbf{X}_1 = -\frac{1}{T} \nabla \mu$ with the generalized potential μ (contains chemical as well as electrical potentials) and a heat current \mathbf{J}_2 due to the force $\mathbf{X}_2 = \nabla \frac{1}{T}$. According to those definition we get from (10.15)

$$\mathbf{J}_1 = -\frac{1}{T} Z_{11} \nabla \mu + Z_{12} \nabla \frac{1}{T} , \quad (10.17)$$

$$\mathbf{J}_2 = -\frac{1}{T} Z_{21} \nabla \mu + Z_{22} \nabla \frac{1}{T} . \quad (10.18)$$

In case of vanishing particle currents $\mathbf{J}_1 = 0$ it follows from (10.17) the identity

$$\frac{1}{T} Z_{11} \nabla \mu = Z_{12} \nabla \frac{1}{T} \quad (10.19)$$

and, using Onsager's relation and reformulating (10.18) with (10.19), for the heat current

$$\mathbf{J}_2 = \left(Z_{22} - \frac{(Z_{12})^2}{Z_{11}} \right) \nabla \frac{1}{T} . \quad (10.20)$$

In the absence of any further perturbations like chemical or electrical potentials from outside ($\mu = 0$) we find

$$\mathbf{J}_2 = Z_{22} \nabla \frac{1}{T} = Z_{22} \left(-\frac{1}{T^2} \nabla T \right) . \quad (10.21)$$

Comparing this result to Fourier's Law (10.7) one finds for the heat conductivity

$$\kappa = \frac{Z_{22}}{T^2}. \quad (10.22)$$

For a microscopical theory of the heat conductivity it remains to compute the response coefficients Z_{ij} .

10.4.2. Transport Coefficient

In case of an electric perturbation of a system Kubo was able to derive a formula for the conductivity tensor $\sigma_{ij}(\omega)$ by first order perturbation theory. Thereby he considered the external electric potential given as an operator part within the Hamiltonian of the system. The result of this consideration is basically a current-current autocorrelation function

$$\sigma_{ij}(\omega) = \int_0^\infty dt e^{i\omega t} \int_0^\beta d\lambda \text{Tr} \{ \mathbf{J}_j(-t - i\hbar\lambda) \mathbf{J}_i \rho_0 \}, \quad (10.23)$$

with the frequency ω of the perturbation and ρ_0 being the equilibrium state of the system at inverse temperature β (cf. [81]). The current operators are here in the Heisenberg picture, i.e., for a system with an unperturbed Hamiltonian \hat{H} defined as

$$\mathbf{J}(x) := e^{\frac{i}{\hbar} \hat{H} x} \mathbf{J} e^{-\frac{i}{\hbar} \hat{H} x}. \quad (10.24)$$

Since the above Kubo formula essentially consists of a current-current autocorrelation, it may ad hoc be transferred to heat transport simply by replacing the electrical current by a heat current [95]. However, the justification of this replacement remains a conceptual problem since there is no way of expressing a temperature gradient⁶ in terms of an addend to the Hamiltonian. Remarkably enough, Kubo himself comments on that replacement in a rather critical way⁷.

At least Luttinger proposed a formula for the response coefficient⁸ for ther-

⁶“...to obtain, say, the thermal conductivity, there exists no mechanical formulation, since there is no Hamiltonian which describes a thermal gradient.” (Luttinger, [95, p.A1505])

⁷“Therefore, the treatment developed ...[above] does not seem to be directly applicable to nonequilibrium states produced by such thermal forces, in order to obtain explicit formulas expressing the responses to thermal forces. It is generally accepted, however, that such formulas exist and are of the same form as those for responses to mechanical disturbances.” (Kubo, [82, p.183])

⁸“Although these derivations are not as rigorous as Kubo's mechanical one, they are quite plausible, and there has been little doubt that the resulting formulas are correct.” (Luttinger, [95, p.A1506])

mal perturbations on the basis of Kubo's theory finding

$$Z_{22} = \lim_{s \rightarrow 0} \int_0^\infty dt e^{-st} \int_0^\beta d\lambda \text{Tr} \{ \mathbf{J}(-t - i\hbar\lambda) \mathbf{J} \rho_0 \} . \quad (10.25)$$

Additionally, one needs the limit of $\omega \rightarrow 0$ here since a frequency dependent thermal perturbation seem even more questionable than the analogy to electric perturbations. The exponential function here with $s > 0$ is a switch on function of the perturbation from the infinite past, to guarantee the convergence of the integral. For a more detailed derivation of such correlation functions see Sect. 13.4.

There are some further discussions about the divergence of the response coefficient for $\omega \rightarrow 0$ and the respective weight of the delta-function (so called Drude-weight) as well as the regular part inside the above formula. But these discussions are definitely beyond the scope of this text and we therefore refer to some further literature only (see e.g. [59]).

Since there is no detailed derivation based on assumptions or preconditions, it is hard to state the limits of applicability of the formula clearly. Despite all these insufficiencies of this approach, it has become a widely employed technique and it allows for a straightforward application to any system, once it is partially diagonalized [61, 79, 157].

10.5. Survey of Recent Developments

During the past decade or so the established field of “heat transport” has enjoyed a come-back within the physical community. This is not only a consequence of the conceptual difficulties of the above described standard microscopical approaches – the Peierls-Boltzmann theory and the Green-Kubo formula – but is also a result of some new and even technical developments.

In a time where electronic circuits and mainly computer chips are getting smaller and smaller, the knowledge about *thermodynamic properties on the nanoscale* becomes more and more important. Especially, the quantum limits to some standard thermodynamic concepts may eventually lead to a revolution not only in the theoretical and experimental understanding of the dynamics of small systems, but also in their technical applications. Thus, there is an increasing interest in all experimental as well as theoretical advances concerning heat transport in nanoscopic devices. All together this has led to a revival of the old, but to a certain degree unsolved questions and to a new vital discussion on heat conduction, especially in small quantum systems.

Unfortunately, the microscopic foundation of Fourier's Law seems to be very complicated and far from being trivial as stated by the title of [8], “Fourier's

Law: a challenge to theorist". The numerous difficulties encouraged the authors to promise a bottle of wine⁹ for a proper microscopic theory. Another statement about the actual status of heat conduction research recently appeared in Nature Physics: "No one has yet managed to derive Fourier's Law truly from fundamental principles" [14]. However, we hope to convince the reader in the present Part II of this text that there are several ideas of how to approach normal heat conduction and thus Fourier's Law from quantum mechanics directly.

The following selection of heat conduction research does not review the contents of the respective approach nor claims any completeness. It is only meant to show the great variety of different ideas and their links to our work.

10.5.1. Heat Conduction in Classical Systems

Since the work at hand is mainly based on quantum mechanical ideas, we briefly comment on classical models of heat conduction, only. We refer the interested reader to the excellent review article [88], which summarizes the central techniques and the main results of heat conduction based on classical mechanics.

In the classical domain it seems to be largely accepted that normal transport requires chaotic microscopic dynamics¹⁰ whereas ballistic transport is typically to be found in completely integrable systems following a regular dynamics (cf. [17, 117]). Therefore, one finds, e.g. a normal transport in a Lorentz gas [84, 152] model which is strongly chaotic (of course, the heat transport is strictly connected to particle diffusion, here). However, there have also been successful attempts to observe normal transport in the absence of exponential instability (cf. [89]), i.e. without chaos.

Considering the many different strange model systems one gets the impression that it is really hard to find the desired diffusive behavior. This contradicts our all day experience, since normal diffusion seems to be the typical property rather than ballistic behavior. Nevertheless, people proposed several "spring and ball" models combined with classical free particle models and different masses etc. ("ding-a-ling"-model [17], "ding-a-dong"-model [118]) to finally obtain normal transport behavior. Furthermore, there are lots of other models, e.g. chains of nonlinear oscillators, see [23, 35, 70, 86, 87, 126].

⁹"This is what we would consider a satisfactory answer to the challenge in the title of this article and we offer a bottle of very good wine to anyone who provides it." (Bonetto et al. in [8])

¹⁰Chaotic dynamics is typically combined with nonintegrability.

10.5.2. Experimental Investigations

Recently, there have been some efforts to measure the heat conductivity of a single carbon nanotube. Besides some evidences of ballistic phonon transport in nanotubes [19, 155], there are measurements on the length and temperature dependence of the heat conductivity, see e.g. [34], too.

Furthermore, there are several investigations on the thermal conductance of magnetic systems. Most of those materials are insulators, where the heat transport is not dominated by electrons, and related to high temperature superconductivity. Inside of such materials one frequently finds chains, ladders or quasi two dimensional spin structures. Thus, besides the standard phonon induced heat transport in insulators, also magnons could be involved. A characteristic of such a behavior is the large anisotropy between the thermal conductivity measured parallel to spin structures and perpendicular to it. Furthermore, the absolute value of the heat conductivity in some insulating compounds is extremely high, and comparable with the conductivity of metals. This has led to the assumption of ballistic magnon transport in such materials. For an overview on important measurements see [59] and for recent experimental results [67, 68, 119, 141–144].

10.5.3. Quantum Mechanical Approaches

Kubo-Formula (Static): To support the experimental results of the last Section there are several efforts to evaluate the thermal Kubo-formula for spin structures. Despite the above discussed shortcomings of the Kubo-formula, it is, nevertheless, a frequently used technique to account for the thermal conductivity of a system. Furthermore, it allows for a discussion of the emergence of regular transport, scaling properties of the conductivity and temperature dependencies. Besides some analytical attempts for integrable systems [157, 158], there are numerous numerical ones, e.g. [59–63, 78, 79], computing the Kubo-formula for several concrete spin systems. An important quantity is the Drude weight, i.e. the conductivity for frequency zero. A divergent weight indicates ballistic transport. One promising method evaluates the whole frequency dependent conductivity first, a set of delta-peaks with different weights for finite systems. Sorting those peaks into bins and estimating the value for frequency going to zero gives the desired conductivity (see [62, 72]).

The big advantage of the Kubo formula refers to its computability for a concrete model having partially diagonalized its Hamiltonian. However, it comes without any criteria for its applicability, thus, possibly leading to wrong results. According to the theory presented in this text it seems to be possible to base the Kubo formula for thermal transport on first principles (see [42]).

Reservoir Coupling (Dynamical): Essentially, the Kubo formula is based on the linear response theory. In order to derive the proper equation, the external perturbation has to be formulated as a potential part in the Hamiltonian of the system. As discussed above this is not possible for thermal perturbations. To overcome this problem such Kubo-scenarios have recently been transferred from Hilbert to Liouville space, where temperature gradients may be formulated in terms of operators [103] (see also Chap. 12). In such approaches several heat reservoirs are coupled to the system described by a quantum master equation. Numerically, the method reveals normal heat transport in the final stationary local equilibrium state [105, 121–125] in surprisingly small quantum systems. Furthermore, there are some attempts to solve such bath scenarios analytically, e.g. for the Ising model [85].

Another approach, by coupling the system to heat baths of different temperatures, refers to the Landauer-Büttiker formula [83]. The system is considered as a junction, e.g. a small molecule, which transmits or reflects incoming modes from the two reservoirs of different temperature. The heat flow is thus only defined by the transmitted modes. Again the model reveals both normal and ballistic transport in dependence of the type of the junction [136–138]. However, since the system does not contain an internal topological substructure, there is no room for getting Fourier’s Law inside the system proper.

Instead of the coupling to reservoirs of different temperature in Liouville space, there are proposals to impose a current inside the system by adding the standard current operator (see Sect. 11.1) to the Hamiltonian of the system [2, 3, 28]. Finally, one observes again the quasi stationary state in the system finding domains of normal respectively ballistic transport in spin chains.

Quantum Chaos: As in the classical domain there are some investigations on the relation between regular transport and the onset of quantum chaos, too. Since the Schrödinger equation is a linear equation of motion, the chaos debate in quantum mechanics and the onset of “quantum chaos” itself is an open question at the moment. However, Mejia-Monasterio et al. [98] have recently found some evidences of chaotic behavior of a spin chain model under a heat conducting bath coupling. Passing from ballistic to regular transport by changing a single system parameter, the system fades from an integrable model into a chaotic one. This onset of quantum chaos is observed by the change in the level distribution form a Poissonian into a Wigner-Dyson type of distribution (cf. [49]). Since the new theory presented in the text at hand allows for a more detailed discussion of the emergence of regular respectively ballistic transport, there are some attempts to find correlations between the change of the level statistic of a system and its transport behavior [145].

11. Heat Current

A meaningful definition of heat flux requires some care since it involves the transformation of an implicit “mesoscopic” definition into a workable microscopic definition.

S. Lepri, R. Livi and A. Politi in [88]

In order to approach the celebrated Fourier’s Law from quantum dynamics, we investigate the temperature gradient inside, and the heat respectively energy current through a system. In quantum mechanics we would prefer to formulate such observables as an operator applicable to any state of the system. Since the expectation value of local energy is combined with the local Hamiltonian of the system, the energy gradient, i.e. the difference of local energies is easily formulated as an operator. We may directly use the local energy and, furthermore, the local temperature as discussed in Chap. 4. Thus, we concentrate on the energy respectively heat current in a quantum system in the following.

For the proper investigation of local behavior in a quantum system, the system has to feature a topological structure in real space as introduced in Sect. 2.1. Such a structured system can then be coupled at the edges to heat baths of different temperatures. The effect of the latter could be modeled by a quantum master equation, using the dissipators deduced in Sect. 3.4. Because of the coupling to heat reservoirs of *different temperature* the system enters, after some relaxation time, a *stationary local equilibrium state*. In contrast to the global equilibrium state, it is not feasible to define a global temperature within the system. The temperature just varies locally. Anyhow, the subunits proper reach an equilibrium state according to a *local* temperature. Globally, the system thus contains a temperature gradient and due to the external force also a stationary heat current.

To characterize the stationary nonequilibrium situation we first have to define the mentioned current operator. In the following we will discuss some properties of this operator, especially whether or not the current is a conserved quantity. In the last Section of this Chapter we will attempt an interpretation in terms of quasiparticles and discuss the related difficulties.

11.1. Current Operator

For a system consisting of several subunits and a Hamiltonian like (2.1), we think of all energy concentrated in the local part of the Hamiltonian of the system, only a small amount being in the interaction (weak coupling limit). As already discussed this kind of limitation is necessary to make the partition of the system into subunits sensible and to allow for a suitable local temperature definition.

In order to gain an operator for the current¹ between two adjacent subunits in our system, we consider the time evolution of the local energy operator given by the Heisenberg equation of motion for operators at site μ (cf. [40, 121, 157])

$$\frac{d}{dt} \hat{H}_{\text{loc}}(\mu) = \frac{i}{\hbar} [\hat{H}, \hat{H}_{\text{loc}}(\mu)] + \frac{\partial \hat{H}_{\text{loc}}(\mu)}{\partial t}. \quad (11.1)$$

Since here and in the following the local Hamiltonian does not depend on time the last term vanishes. Plugging in the complete Hamiltonian (2.1), one immediately finds

$$\frac{d}{dt} \hat{H}_{\text{loc}}(\mu) = \frac{i}{\hbar} \left[\sum_{\mu=1}^N \hat{H}_{\text{loc}}(\mu) + \frac{\lambda}{\lambda_0} \sum_{\mu=1}^{N-1} \hat{H}_{\text{int}}(\mu, \mu+1), \hat{H}_{\text{loc}}(\mu) \right]. \quad (11.2)$$

The local Hamiltonian commutes with the complete local part of the Hamiltonian and almost all interaction operators. The non-commuting part of the interaction has to contain operators acting on subsystem μ . Thus, we are left with

$$\frac{d}{dt} \hat{H}_{\text{loc}}(\mu) = \frac{i}{\hbar} \frac{\lambda}{\lambda_0} \left([\hat{H}_{\text{int}}(\mu-1, \mu), \hat{H}_{\text{loc}}(\mu)] + [\hat{H}_{\text{int}}(\mu, \mu+1), \hat{H}_{\text{loc}}(\mu)] \right). \quad (11.3)$$

As far as the local energy is a conserved quantity, this equation may be rewritten as

$$\frac{d}{dt} \hat{H}_{\text{loc}}(\mu) = \text{div} \hat{J} = \hat{J}(\mu, \mu+1) - \hat{J}(\mu-1, \mu), \quad (11.4)$$

where we have introduced the discrete version of the continuity equation. Thus, the right hand side of (11.3) can be interpreted as a current into as well as out of the central subunit μ and, thus, we define the current operator as

$$\hat{J}(\mu, \mu+1) = \frac{i}{\hbar} \frac{\lambda}{\lambda_0} [\hat{H}_{\text{int}}(\mu, \mu+1), \hat{H}_{\text{loc}}(\mu)]. \quad (11.5)$$

¹The heat current is already introduced in classical considerations by using an equation of continuity for the local energy, see [20, 88].

The first part on the right hand side of (11.3) is the current from site $\mu - 1$ into site μ and should – under stationary conditions – simply be the negative of the current flowing out of site $\mu - 1$. Likewise we find

$$\begin{aligned}\hat{J}(\mu - 1, \mu) &= \frac{i}{\hbar} \frac{\lambda}{\lambda_0} [\hat{H}_{\text{int}}(\mu - 1, \mu), \hat{H}_{\text{loc}}(\mu - 1)] \\ &= -\frac{i}{\hbar} \frac{\lambda}{\lambda_0} [\hat{H}_{\text{int}}(\mu - 1, \mu), \hat{H}_{\text{loc}}(\mu)] .\end{aligned}\quad (11.6)$$

It turns out that this is only consistent for symmetric interactions and systems consisting of identical subunits, i.e. approximately identical local Hamiltonians. Thus, we have to require that

$$[\hat{H}_{\text{int}}(\mu, \mu + 1), \hat{H}_{\text{loc}}(\mu) + \hat{H}_{\text{loc}}(\mu + 1)] \approx 0 .\quad (11.7)$$

In both special cases of homogeneous Heisenberg as well as Förster coupled chains the concrete current operator² in terms of Pauli operators reads

$$\begin{aligned}\hat{J}(\mu, \mu + 1) &= \frac{i}{\hbar} \frac{\lambda}{\lambda_0} [\hat{H}_{\text{F}}(\mu, \mu + 1), \hat{H}_{\text{loc}}(\mu)] \\ &= \frac{i}{\hbar} \frac{\lambda}{\lambda_0} \left(\hat{\sigma}_+(\mu) \hat{\sigma}_-(\mu + 1) - \hat{\sigma}_-(\mu) \hat{\sigma}_+(\mu + 1) \right) ,\end{aligned}\quad (11.8)$$

according to the definition of the complete Hamiltonian.

Following standard definitions the expectation value of the current for the system in state $\hat{\rho}$ is defined as

$$J = \text{Tr} \{ \hat{J}(\mu, \mu + 1) \hat{\rho} \} .\quad (11.9)$$

For $\hat{\rho} = \hat{\rho}_{\text{st}}$ being the stationary *local* equilibrium state of the system one finds a stationary current inside the material according to (11.9).

Furthermore, we may define a symmetrized current operator to investigate systems with a generalized, eventually asymmetric interaction. Considering instead of the time evolution of the local energy the energy difference between two adjacent sites (cf. (4.30))

$$\frac{d}{dt} \left(\frac{\Delta \hat{H}_{\text{loc}}(\mu, \mu + 1)}{2} \right) = \frac{1}{2} \left(\frac{d\hat{H}_{\text{loc}}(\mu)}{dt} - \frac{d\hat{H}_{\text{loc}}(\mu + 1)}{dt} \right)\quad (11.10)$$

²In this special situation some researchers talk of this current to be the spin current. But for a very large local field in comparison with the interaction this current should be the main energy transporting current and thus approximately the energy current.

one could define the symmetrized current operator as

$$\hat{J}_{\text{sym}}(\mu, \mu + 1) = \frac{i}{2\hbar} \frac{\lambda}{\lambda_0} [\hat{H}_{\text{int}}(\mu, \mu + 1), \Delta \hat{H}_{\text{loc}}(\mu, \mu + 1)] . \quad (11.11)$$

There is yet another possibility to account for the current flowing through the system due to the coupling to heat reservoirs of different temperature. The Liouville-von-Neumann equation of the system (cf. (3.32)) reads

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \hat{\mathcal{L}}_{\text{E}} \hat{\rho} . \quad (11.12)$$

By multiplying with the system Hamiltonian and taking the trace one gets

$$\begin{aligned} \text{Tr}\{\hat{H} \frac{\partial \hat{\rho}}{\partial t}\} &= \frac{\partial}{\partial t} \text{Tr}\{\hat{H} \hat{\rho}\} = -\frac{i}{\hbar} \text{Tr}\{\hat{H} [\hat{H}, \hat{\rho}]\} + \text{Tr}\{\hat{H} (\hat{\mathcal{L}}_{\text{E}} \hat{\rho})\} \\ &= \text{Tr}\{\hat{H} (\hat{\mathcal{L}}_{\text{E}} \hat{\rho})\} , \end{aligned} \quad (11.13)$$

where $\hat{\mathcal{L}}_{\text{E}}$ refers to the reservoir dissipator. The change of the total energy in the system is thus given by (11.13). Therefore, we could define the expectation value of the energy current as

$$J = \text{Tr}\{\hat{H} (\hat{\mathcal{L}}_{\text{E}} \hat{\rho})\} . \quad (11.14)$$

11.2. Conserved Quantities

The complete current operator may be a conserved quantity of the considered system $[\hat{H}, \hat{J}] = 0$. That means that a current once prepared in a closed loop of such a material will never vanish. Thus, there is no finite conductivity and Fourier's Law cannot be fulfilled. Such a transport behavior is called *ballistic transport*. A famous example in this context is the harmonic chain which does not feature any resistance for the energy current. As previously discussed, in solid state theories one needs anharmonic potentials to overcome this problem and to implement a finite heat conductivity in a crystal. As long as we imagine the heat current as a quasiparticles transport problem (phonons, magnons), these potentials are interpreted to give rise to scattering processes for the respective quasiparticles in the crystal (see Sect. 10.3).

In both the Heisenberg and the Förster model, we now investigate whether the current is a conserved quantity or not, especially depending on the commutators $[\hat{H}_{\text{loc}}, \hat{J}(\mu, \mu + 1)]$, $[\hat{H}_{\text{F}}, \hat{J}(\mu, \mu + 1)]$ and $[\hat{H}_{\text{NR}}, \hat{J}(\mu, \mu + 1)]$. Firstly,

concentrating on the local part of the Hamiltonian, this could only be non zero for the part of \hat{H}_{loc} concerning the site μ respectively $\mu + 1$, finding

$$\begin{aligned} [\hat{H}_{\text{loc}}, \hat{J}(\mu, \mu + 1)] &= [\hat{H}_{\text{loc}}(\mu) + \hat{H}_{\text{loc}}(\mu + 1), \hat{J}(\mu, \mu + 1)] \\ &= [\hat{H}_{\text{loc}}(\mu), \hat{J}(\mu, \mu + 1)] + [\hat{H}_{\text{loc}}(\mu + 1), \hat{J}(\mu, \mu + 1)] . \end{aligned} \quad (11.15)$$

Keeping in mind that local parts of the Hamiltonian commute among each other, we find for the second commutator

$$\begin{aligned} [\hat{H}_{\text{loc}}(\mu + 1), \hat{J}(\mu, \mu + 1)] &\propto [\hat{H}_{\text{loc}}(\mu + 1), [\hat{H}_{\text{int}}(\mu, \mu + 1), \hat{H}_{\text{loc}}(\mu)]] \\ &= [\hat{H}_{\text{loc}}(\mu), [\hat{H}_{\text{int}}(\mu, \mu + 1), \hat{H}_{\text{loc}}(\mu + 1)]] . \end{aligned}$$

According to (11.6) the internal commutator is simply $-\hat{J}(\mu, \mu + 1)$ and therefore, plugging in all these findings into (11.15) it is shown that the current always commutes with the local part of the Hamiltonian.

Secondly, we consider the concrete Heisenberg respectively Förster interaction and thus the current operator (11.8) in a loop system. Summing over all commutators for all currents $\hat{J}(\mu, \mu + 1)$ between two subsystems, we find

$$\sum_{\mu} [\hat{H}_{\text{F}}, \hat{J}(\mu, \mu + 1)] = 0 , \quad \sum_{\mu} [\hat{H}_{\text{NR}}, \hat{J}(\mu, \mu + 1)] \neq 0 , \quad (11.16)$$

skipping here the rather lengthy calculation. This means that for a chain, which is coupled by a Förster type interaction (energy transfer interaction) only, there is no finite conductivity because the current is a conserved quantity. But, if the system is coupled, additionally, with a non-resonant interaction, a finite heat conductivity is possible.

For random couplings, it is unlikely that the interaction commutes with the current operator. Thus, we expect to find regular transport under such conditions.

11.3. Quasiparticle Interpretation

A well-established classical picture for heat conduction in insulators refers to quasiparticle induced transport. Usually, phonons are thought to be responsible for the transport of heat through insulators. On their paths, phonons are scattered at impurities or boundaries of the solid and even at each other, loosing energy (dissipation). Obviously, this suggest phonons to be a “gas” of classical particles.

Within the Peierls-Boltzmann theory of transport there is one central assumption – the Stoßzahlansatz. By neglecting correlations of the scattered

particles after the collision, the scattering process can be described by a rate equation (molecular chaos), i.e. the phonon needs to be scattered statistically into a suitable number of other modes. As a consequence one needs a not too small system to justify the respective assumption. Since we are mainly interested in small systems, basically consisting of only a few subunits where such a rate equation description seems questionable, we will not waste much space for considerations on quasiparticles. However, let us shortly discuss some central properties of the quasiparticle picture here, since it is very familiar to most physicists.

The goal of all further efforts is to approach a quasiparticle Hamiltonian from a low level starting point, e.g. a harmonic chain or a Heisenberg spin chain. Maybe, this new Hamiltonian could be produced by an, in some sense, exact transformation of the initial Hamiltonian or by a suitable approximation scheme, e.g. a low temperature approximation. Having identified a suitable quasiparticle, we will interpret the transport properties according to the Peierls-Boltzmann theory, i.e. treat the quasiparticles as a classical dilute gas with defined particle velocities and a scattering according to a rate equation. Thus, it is at least important to keep some scattering terms in the quasiparticle Hamiltonian for the emergence of regular heat transport.

11.3.1. Harmonic Chain

The most simple model for a one dimensional solid is the harmonic chain (N sites), based on the well-known Hamiltonian

$$\hat{H} = \frac{1}{2} \sum_{\mu=1}^N (\hat{p}_\mu^2 + (\hat{q}_{\mu+1} - \hat{q}_\mu)^2) \quad (11.17)$$

with periodic boundary conditions. Here, we have chosen for simplicity the masses, spring constants as well as the distance of masses equal to one. Following Kittel [76], one performs the Fourier transformation

$$\hat{q}_\mu = \frac{1}{\sqrt{N}} \sum_k \hat{Q}_k e^{ik\mu}, \quad \hat{p}_\mu = \frac{1}{\sqrt{N}} \sum_k \hat{P}_k e^{ik\mu}, \quad (11.18)$$

where the sum runs over all $k = 2\pi n/N$ for a discrete set of values $n \in \mathbb{N}$. Furthermore, we introduce creation and annihilation operators for the quasiparticles

$$\hat{a}_k^\dagger = \frac{1}{\sqrt{2\omega_k}} (\omega_k \hat{Q}_{-k} - i \hat{P}_k), \quad \hat{a}_k = \frac{1}{\sqrt{2\omega_k}} (\omega_k \hat{Q}_k + i \hat{P}_{-k}), \quad (11.19)$$

fulfilling Bose commutation relations $[\hat{a}_k, \hat{a}_{k'}^\dagger] = \delta_{kk'}$. Plugging those operators into (11.17) one finds the diagonal Hamiltonian of the system to be

$$\hat{H} = \sum_k \omega_k \left(\hat{a}_k^\dagger \hat{a}_k + \frac{1}{2} \right), \quad (11.20)$$

with the standard dispersion relation $\omega_k^2 = 2(1 - \cos k)$. The quasiparticles are called phonons, thus \hat{a}_k^\dagger creates a phonon in the mode k whereas \hat{a}_k annihilates one. Obviously, this Hamiltonian contains no interaction terms between the quasiparticles in mode k and any other mode. Therefore we do not expect regular transport in harmonic systems according to Peierls.

11.3.2. Heisenberg Chain

Next, we consider the Heisenberg Hamiltonian, introduced in Sect. 2.1. However, we keep the constants C_F and C_{NR} open to discriminate between terms belonging to Förster respectively non-resonant interaction. Without loss of generality we may furthermore choose $\lambda/\lambda_0 = 1$, absorbing the coupling strength into C_F and C_{NR} . Using some standard properties of the Pauli operators, e.g. $\hat{\sigma}_z = [\hat{\sigma}_+, \hat{\sigma}_-]$, and skipping all constant terms, the Hamiltonian yields

$$\begin{aligned} \hat{H} = & \sum_\mu \left\{ (2 - 4C_{NR}) \hat{\sigma}_+(\mu) \hat{\sigma}_-(\mu) \right. \\ & + \frac{C_F}{2} (\hat{\sigma}_+(\mu) \hat{\sigma}_-(\mu+1) + \hat{\sigma}_-(\mu) \hat{\sigma}_+(\mu+1)) \\ & \left. + 4C_{NR} \hat{\sigma}_+(\mu) \hat{\sigma}_+(\mu+1) \hat{\sigma}_-(\mu) \hat{\sigma}_-(\mu+1) \right\}. \end{aligned} \quad (11.21)$$

Obviously, the last term is of forth order in the operators.

The operators $\hat{\sigma}_+$ and $\hat{\sigma}_-$, sometimes called Jordan-Wigner matrices (see [76]), fulfill anti-commutator relations $[\hat{\sigma}_+(\mu), \hat{\sigma}_-(\mu')]_+ = \delta_{\mu\mu'}$, thus being fermionic creation respectively annihilation operators. The Fourier transformation (distance between adjacent subunits set equal to one)

$$\hat{\sigma}_-(\mu) = \frac{1}{\sqrt{N}} \sum_k e^{ik\mu} \hat{c}_k, \quad \hat{\sigma}_+(\mu) = \frac{1}{\sqrt{N}} \sum_k e^{-ik\mu} \hat{c}_k^\dagger, \quad (11.22)$$

leads to the Hamiltonian

$$\hat{H} = \sum_k \omega_k \hat{c}_k^\dagger \hat{c}_k + \frac{4C_{NR}}{N} \sum_{k_1, k_2, k_3, k_4} \delta_{k_1+k_2, k_3+k_4} e^{i(k_2-k_4)} \hat{c}_{k_1}^\dagger \hat{c}_{k_2}^\dagger \hat{c}_{k_3} \hat{c}_{k_4}, \quad (11.23)$$

an exact result without any approximation. Essentially, the transformed Hamiltonian consists of two parts: A diagonal one according to a dispersion relation ω_k , to which all different terms in the original Hamiltonian contribute and a mode coupling due to the non-resonant interaction, only. The delta function in the coupling describes the momentum conservation in the scattering processes and derives from the fermionic commutation relation

$$\begin{aligned} [\hat{c}_k, \hat{c}_{k'}^\dagger]_+ &= \frac{1}{N} \sum_{\mu\mu'} e^{ik\mu} e^{-ik'\mu'} [\hat{\sigma}_+(\mu), \hat{\sigma}_-(\mu')]_+ \\ &= \frac{1}{N} \sum_{\mu} e^{i(k-k')\mu} = \delta_{kk'} . \end{aligned} \quad (11.24)$$

Obviously, for $C_{\text{NR}} = 0$, i.e. a chain without a non-resonant coupling (Förster chain), we get a diagonal Hamiltonian in such fermionic operators

$$\hat{H} = \sum_k \omega_k \hat{c}_k^\dagger \hat{c}_k . \quad (11.25)$$

One could be tempted to interpret the above result in terms of the Peierls-Boltzmann theory: Since we do not get any interaction between different modes in the Förster chain (11.25), there is no regular heat transport expected. However, in case of an additional non-resonant interaction a mode coupling is present (11.23) and therefore a finite conductivity is feasible. This qualitative result is more or less the same as our result presented later in this text, but obtained from entirely different methods.

In comparison to the harmonic chain in the last paragraph the above Hamiltonian also contains terms of creation and annihilation operators. However, the operators do not fulfill Bose commutation relations as for the harmonic chain, but fermionic ones. This immediately leads to some problems, since the respective system cannot easily be interpreted in terms of quasiparticles like magnons, proper. Fermionic quasiparticles are more complicated than bosonic ones due to the Pauli principle. Thus, such simple-minded ideas of quasiparticles being classical (localized) objects as used in the Peierls-Boltzmann theory seem to be highly dangerous in this context. To overcome this problem let us search for a bosonic picture for the Heisenberg Hamiltonian, as well. This is not an entirely new idea³, but nevertheless useful to gain a better understanding of transport processes.

The lowest lying energy levels of the respective system feature a wavelike character and could be described in a *magnon* picture, as first discussed by

³Considering for example phonon scattering processes at impurities as mode coupling terms in the Hamiltonian (see [99–101]).

Bloch⁴. In order to investigate those lowest excitations of the system we approximate the Hamiltonian in an appropriate way (low temperature approximation). It is convenient to use the Holstein-Primakoff [69] transformation

$$\hat{\sigma}_+(\mu) = \hat{\phi}(\mu) \hat{a}(\mu), \quad (11.26)$$

$$\hat{\sigma}_-(\mu) = \hat{a}^\dagger(\mu) \hat{\phi}(\mu), \quad (11.27)$$

$$\hat{\phi}(\mu) = \sqrt{1 - \hat{n}(\mu)} \quad \text{with} \quad \hat{n}(\mu) = \hat{a}^\dagger(\mu) \hat{a}(\mu), \quad (11.28)$$

to get a set of independent creation and annihilation operators $\hat{a}(\mu)$, $\hat{a}^\dagger(\mu)$ (see [76]). Those operators commute according to $[\hat{a}(\mu), \hat{a}^\dagger(\nu)] = \delta_{\mu\nu}$, thus being creation and annihilation operators for bosons. This transformation is suitable for weakly interacting subunits compared to the local Hamiltonian (see [24]). Furthermore one finds $\hat{\sigma}_z(\mu) = 1/2 - \hat{n}(\mu)$.

For low temperatures, the expectation value of a spin flip is extremely small, thus $\langle \hat{n}(\mu) \rangle \ll 1$. Therefore, we may truncate the expansion of the operator function $\hat{\phi}(\mu)$ in the Holstein-Primakoff transformation as

$$\hat{\phi}(\mu) \approx 1 - \frac{1}{2} \hat{n}(\mu). \quad (11.29)$$

Again, we use the Fourier transformation to switch to the mode operators

$$\hat{b}_k = \frac{1}{\sqrt{N}} \sum_{\mu} e^{ik\mu} \hat{a}(\mu), \quad \hat{b}_k^\dagger = \frac{1}{\sqrt{N}} \sum_{\mu} e^{-ik\mu} \hat{a}^\dagger(\mu), \quad (11.30)$$

with the number of subunits being N and the distance between adjacent subunits equal to one. The new operators fulfill Bose commutation relations, too, therefore defining a quasiparticle with dispersion relation ω_k – the magnon. Finally, one finds the lowest order of the approximated Hamiltonian to be

$$\hat{H}_0 = \sum_k (C_F \cos k - 1 - C_{NR}) \hat{b}_k^\dagger \hat{b}_k = \sum_k \omega_k \hat{b}_k^\dagger \hat{b}_k. \quad (11.31)$$

Unlike (11.23) this result is not exact.

Considering the next higher order of the expansion, we get some further

⁴“Bloch invented the concept of spin wave which consists of a single reversed spin coherently distributed over a large number of otherwise aligned atomic spins in a crystal lattice.” (Dyson in [24, p.1217], see also [6])

terms describing magnon scattering processes

$$\begin{aligned} \hat{H}_1 = & \frac{C_{\text{NR}}}{N} \sum_{k_1, k_2, k_3, k_4} \delta_{k_1+k_2, k_3+k_4} e^{i(k_2-k_4)} \hat{b}_{k_1}^\dagger \hat{b}_{k_2}^\dagger \hat{b}_{k_3} \hat{b}_{k_4} \\ & - \frac{C_F}{4N} \sum_{k_1, k_2, k_3, k_4} \delta_{k_1+k_2, k_3+k_4} e^{i(k_2-k_4)} \\ & \times \left(e^{ik_1} + e^{-ik_2} + e^{-ik_3} + e^{ik_4} \right) \hat{b}_{k_1}^\dagger \hat{b}_{k_2}^\dagger \hat{b}_{k_3} \hat{b}_{k_4}. \end{aligned} \quad (11.32)$$

Both the Förster and the non-resonant interaction contribute to the first order scattering term. Thus, the Förster chain should feature regular transport, too, in contrast to the fermionic result. Furthermore, the heat conductivity diverges in both the Förster and the Heisenberg model for low temperatures. This ambiguity reveals the difficulty of the quasiparticle approach according to the Peierls-Boltzmann theory: The final result seriously depends on the chosen quasiparticle. Nevertheless, the latter model is better interpretable due to its bosonic character, than the above fermionic one.

Using the Bethe ansatz it is possible to diagonalize even the complete Heisenberg Hamiltonian (see [4, 73]), which is feasible for any Hamiltonian by a suitable unitary transformation. Thus, an equation like (11.20) should always come in reach. However, the respective operators would not fulfill any defined commutator relation neither bosonic nor fermionic ones. To our understanding, in such general cases there was no adequate interpretation in terms of quasiparticles (with or without scattering) any longer. Such a complete diagonalization is an interesting option, but not suitable for a deeper insight into the physical nature of such a problem like heat transfer. Only in a case where a complete diagonalization is possible in terms of reasonable physical quantities⁵, this could help us to understand the nature of the problem better. Obviously this is the case for the harmonic chain, where the Hamiltonian is diagonal in phonon creation and annihilation operators.

While quasiparticle pictures are eventually useful to gain an intuitive understanding of complicated processes in solids, they must be used with care. However, note that such inconsistencies mainly occur in considerations concerning transport, and not in case of properties depending on partition function or the energy spectrum of quasiparticles only.

⁵In a private conversation with H. Michel the present author was led to the conclusion that one should restrict oneself to transformations conserving the bosonic character of the operators. Including physical facts part by part into the respective quasiparticle, e.g. including the impact of impurities into new “phonons” instead of considering phonon scattering at impurities, one may end up with a diagonal and meaningful Hamiltonian.

12. An Open System Approach to Heat Conduction

The origin of diffusive behavior in thermal conduction, which is formulated in the Fourier heat law, is actively studied by many researchers. Unlike the equilibrium properties ... the Fourier heat law cannot be explained by the harmonic crystal, where the internal temperature gradient is not formed ...

K. Saito, S. Takesue, S. Miyashita in [124]

Having established some tools like the current operator for the observation of nonequilibrium scenarios in quantum mechanics, we are prepared for an investigation of a system-bath model according to a quantum master equation. Recently, in chains of weakly coupled identical subunits as introduced in Sect. 2.1, coupled to heat reservoirs of different temperatures, strong indications for regular heat transport (cf. [105, 121, 124]) have been found. However, the type of transport in such systems depends on the respective coupling of the subunits. Several systems show a normal heat conduction, i.e., one finds both a linear temperature gradient and a heat current inside the system. Finally, this gives rise to a finite conductivity. Some other studies show a completely different behavior with no linear temperature gradient. Instead, the temperature profile flattens which leads to a divergent conductivity – ballistic transport. Here we start with a numerical investigation of the heat transport in small quantum systems within a quantum master equation approach.

12.1. Heat Transport in Low Dimensional Systems

The system under consideration is depicted in Fig. 12.1. It is described by the Liouville-von-Neumann equation

$$\frac{\partial}{\partial t} |\hat{\rho}\rangle = \hat{\mathcal{L}} |\hat{\rho}\rangle = (\hat{\mathcal{L}}_S + \hat{\mathcal{L}}_1(T_1, \lambda_E) + \hat{\mathcal{L}}_2(T_2, \lambda_E)) |\hat{\rho}\rangle \quad (12.1)$$

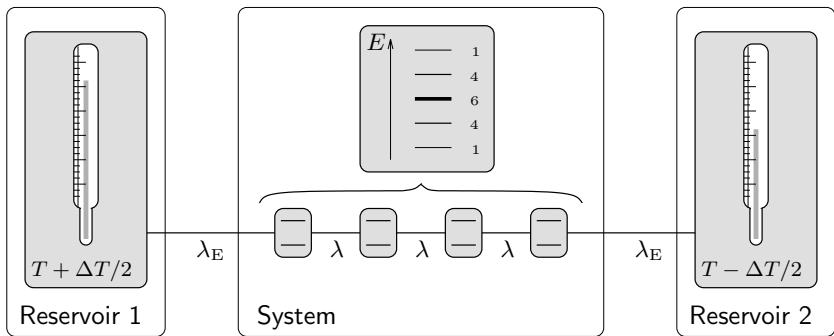


Figure 12.1.: Quantum mechanical heat conduction model system. Several weakly coupled spins (λ) coupled to two heat reservoirs (λ_E) of different temperature modeled by a quantum master equation

with a coherent part $\hat{\mathcal{L}}_S$ and the dissipators¹ $\hat{\mathcal{L}}_i(T_i, \lambda_E)$, see Chap. 2 and Sect. 3.4. The system itself is a chain of $N = 4$ spins weakly coupled by some next neighbor interaction with an internal coupling strength $\lambda = 0.01$. The temperatures of the reservoirs are chosen to be $T_{1(2)} = T + (-)\Delta T/2$, according to a mean temperature $T = 0.15$ and a small temperature difference $\Delta T = 0.05$. Furthermore, a weak coupling is assumed between system and either reservoir with external interaction strength $\lambda_E = 0.01$.

Since the complete super operator $\hat{\mathcal{L}}$ is time independent, the linear system of differential equations is asymptotically stable if all real parts of the eigenvalues of $\hat{\mathcal{L}}$ are less than zero. We find only one eigenvalue which is exactly zero, all others featuring negative real parts. Thus, the system reaches a stationary state, irrespective of the initial state. This stationary state itself is an eigenstate of $\hat{\mathcal{L}}$ belonging to the eigenvalue zero and contains all interesting quantities like currents and temperature gradients.

Here we investigate all three different types of internal couplings between the spins defined in Sect. 2.1 to test the dependence on the interaction. First, we consider the coupling due to an energy transfer only (Förster interaction (2.6)). The two edge spin systems are drawn to the temperatures of their respective bath (cf. Fig. 12.2a), whereas the two systems in the middle are exactly on the same mean temperature T , measured as discussed in Sect. 4.4 in units of the local energy splitting ($\Delta E = 1$). Obviously the gradient in the middle of the system vanishes and, thus, we do not find a normal heat conduction in the system. Of course, the current does not diverge, because it is limited by the resistance of the bath contact, but, nevertheless, Fourier's

¹Here, we use the dissipator (3.33).

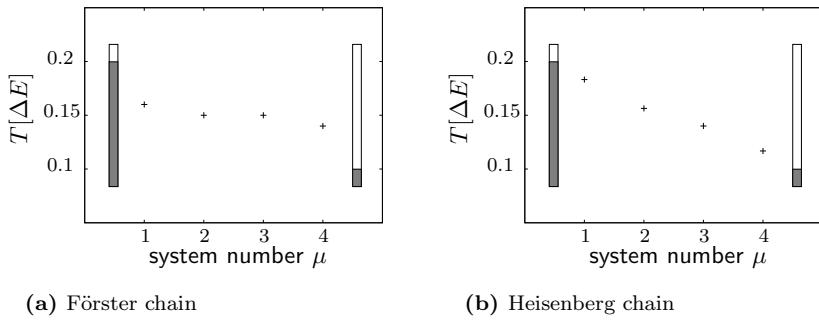


Figure 12.2.: Temperature profile for a spin chain ($N = 4$) coupled to heat baths at both ends (bars in the boxes mark the appropriate temperature of the bath). **(a)** internal next neighbor Förster coupling **(b)** internal next neighbor Förster and non-resonant coupling (Heisenberg interaction).

Law does not seem to be fulfilled in this special coupling scenario.

However, by investigating the Heisenberg coupling model (cf. Sect. 2.1), we find a non vanishing temperature gradient shown in Fig. 12.2b. Before we analyze the Heisenberg chain in more detail in the next Section, we turn to investigate a chain with random next neighbor couplings (2.7). This coupling is chosen to be weak again and we take the same coupling between different pairs of adjacent subunits (i.e. no disorder in the system). The random coupling is supposed to model “typical interactions” without any bias. In this case we find a linear temperature profile as shown in Fig. 12.3, too. Therefore the normal heat conduction seems to be a general result of this special class of models.

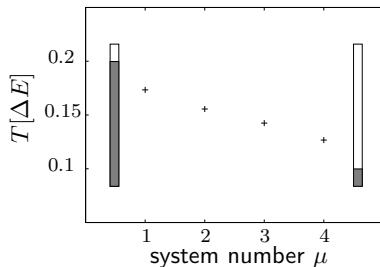


Figure 12.3.: Temperature profile: open system with weak internal random next neighbor coupling.

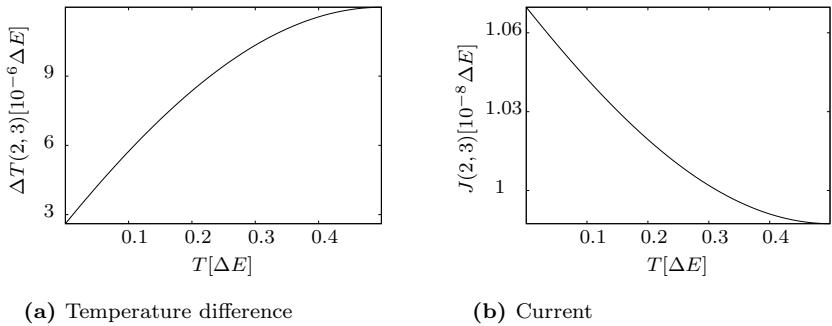


Figure 12.4.: (a) Temperature difference between the two central systems $\Delta T(2, 3)$ of a four spin chain. (b) Current between the two central systems, both as a function of the mean temperature $T(0.00025 \leq T \leq 0.49905)$

12.2. Fourier's Law for a Heisenberg Chain

In the following, we investigate the Heisenberg chain in more detail. In Fig. 12.2b we have found a finite temperature gradient between the two central systems. Since the non-resonant coupling term of the Heisenberg chain is nothing else but a constant local energy displacement in the lowest excitation subspace, it cannot play a crucial role for very low temperatures. Thus, we could state that we will approach a flat profile in this limit, like in Förster coupled chains.

To investigate this feature, we choose a very small temperature difference $\Delta T = 0.0001$ and change the mean temperature within the range $T = 0.00025 \dots 0.49905$. In Fig. 12.4a we show the temperature difference between the two systems in the middle of the chain as a function of the mean temperature T . As expected, the temperature difference vanishes for very low mean temperatures.

Another important quantity refers to the expectation value of the current operator. From the stationary state of the system we can evaluate this current according to (11.5). For the temperature difference between the two baths $\Delta T = 0.0001$ as in the above investigation and for different mean temperatures T , we find that the current increases for lower mean temperatures (see Fig. 12.4b). This is a very small effect, as can be seen from the absolute amount of the increase of the current in comparison to the decrease of the temperature difference. The reason here is, that the current is mainly determined by the contacts of the system to the heat baths. Consequently, the

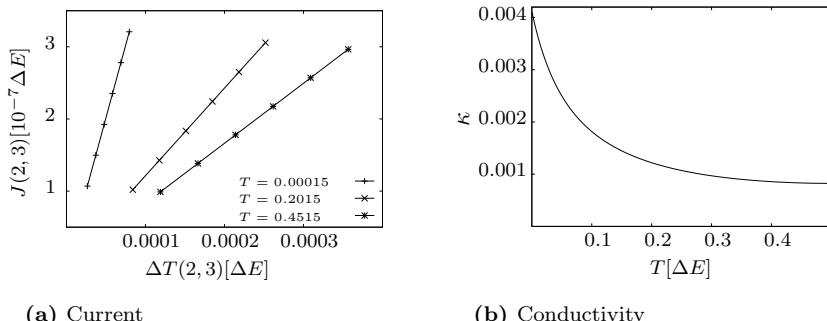


Figure 12.5.: (a) Validity of Fourier's Law: Current over temperature difference between the two central systems $(2, 3)$. The temperature differences of the heat baths are taken at mean temperatures $T = 0.00015, 0.2015, 0.4515$, respectively. **(b)** Dependence of the conductivity κ on the mean temperature.

resistance of these contacts is mainly responsible for the total amount of the current.

Finally, we are interested in the validity of Fourier's Law in this small model system. Thus, we work at three different fixed mean temperatures $T = 0.00015, 0.2015, 0.4515$, for which we change the temperature difference of the two heat baths $\Delta T = 0.001 \dots 0.002$ and compute the current as well as the temperature difference of the two central systems. In Fig. 12.5a we show the current of the local equilibrium state $J(2, 3)$ as a function of the temperature difference between the two central systems. As can be seen, we get a very good linear behavior for each mean temperature and Fourier's Law seems to be fulfilled. The gradient of the straight line defines the conductivity κ , which obviously depends on the mean temperature chosen. In Fig. 12.5b the dependence of the conductivity κ on the mean temperature is depicted over the whole temperature range.

For the overwhelming majority of coupling scenarios we have found a normal heat conduction within our quantum mechanical approach. Even in case of an unbiased random coupling within the considered chains, a local equilibrium behavior and therefore a normal heat conduction shows up. Also in the special case of the Heisenberg coupling we are able to show the validity of Fourier's Law. Only for a very special interaction type – pure Förster interaction – the conductivity diverges and we do not get a normal heat conduction but ballistic transport. As previously discussed we also get a temperature

dependent conductivity κ here. The conductivity increases for low temperatures in a Heisenberg chain. Thus we get a more “ballistic transport” in this temperature regime, as also found from the quasiparticle considerations.

To deduce these results no further assumptions are needed, only the principle of open quantum systems. Furthermore, this approach is valid even for very small systems, like the considered chain models with only four spins, where a quasiparticle approach seems more than problematic.

12.3. Scaling Behavior

So far we have considered the heat conductivity for a chain of four spins only. For the conductivity to be a bulk property of the system we need a linear dependence of the current on the number of subsystems in the chain. The full numerical solution of the problem is rather challenging, since we have to work in full Liouville space. Thus, we restrict ourselves to the stationary current² in systems containing up to six spins. In Fig. 12.6 we show this current over the inverse system size, getting a rather good linear dependence: $J \propto N^{-1}$.

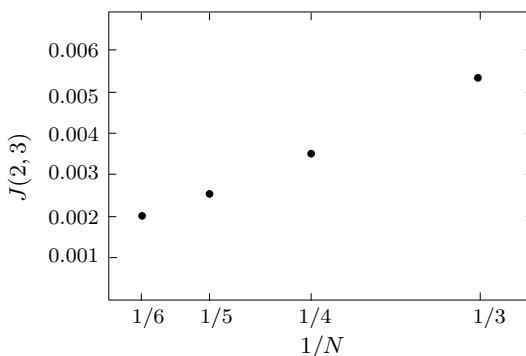


Figure 12.6.: The dependence of the current on the inverse chain length N^{-1} for a Heisenberg chain with $N = 3 - 6$. ($\Delta T = 0.2$, $T = 0.3$)

²Note that we choose some different parameters here: $\Delta T = 0.2$ and $T = 0.3$.

13. Perturbation Theory in Liouville Space

The principal purpose ... is to develop a general scheme for the calculation of kinetic coefficients, or admittance for external forces such as electric or magnetic susceptibility for alternating field, electric conductivity, heat conductivity and so on.

R. Kubo in [81]

Instead of solving the full Liouville-von-Neumann equation as done in the last Chapter it should be highly desirable to have a simple, but consistent perturbation method available. However, as already indicated, the mentioned super operators describing the influence of the environment cannot be written as a potential term in the Hamiltonian of the system. Therefore a theory of linear response in the Hilbert space in terms of the celebrated Kubo formula is not applicable here. To consistently treat heat currents and local temperature gradients quantitatively for thermal perturbations, too, we propose to extend the Kubo technique to Liouville space. Since the Liouvillian is not a standard operator, but a super operator in a higher space acting on the operators of the Hilbert space we first introduce some central properties of those operators.

13.1. Super Operators

In (2.15) we have introduced the so called Liouville operator acting on an operator of the Hilbert space, e.g. the density operator. Following Schack et al. [128], the set of linear operators acting on states of an n -dimensional Hilbert space \mathcal{H} constitute a $d = n^2$ -dimensional complex vector space – the Liouville space \mathcal{L} . Sorting all entries of an operator \hat{A} in \mathcal{H} (e.g. the density operator) into an n^2 -dimensional vector we could define “ket” and “bra” vectors in this super space \mathcal{L} as

$$\hat{A} \Rightarrow |\hat{A}\rangle, \quad \hat{A}^\dagger \Rightarrow (\hat{A}|. \tag{13.1}$$

As a complex vector space one could define an inner product in \mathcal{L} given by the trace-norm of operators in \mathcal{H}

$$\langle \hat{A} | \hat{B} \rangle = \text{Tr}\{\hat{A}^\dagger \hat{B}\}. \quad (13.2)$$

Having defined “states” in the Liouville space which are operators in \mathcal{H} one can also define some operators acting on these states called *super operators*. A super operator $\hat{\mathfrak{A}} = |\hat{A}(\hat{B}|)$ acts on an arbitrary state $|\hat{X}\rangle$ of \mathcal{L} according to

$$\hat{\mathfrak{A}}|\hat{X}\rangle = |\hat{A}\rangle(\hat{B}|\hat{X}\rangle) = \text{Tr}\{\hat{B}^\dagger \hat{X}\}\hat{A}. \quad (13.3)$$

One could think of the super operator simply being represented by an $n^2 \times n^2$ -dimensional matrix in the higher dimensional space, acting on the vectors as defined above.

A complete set of operators $\{|\hat{A}_j\rangle\}$ in \mathcal{H} constitute an operator basis for the Liouville space of the respective system, e.g. for a single spin this could be the set of Pauli operators $\{\hat{\sigma}_0, \hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\}$. In general this set of operators is complete but not orthonormal, i.e. the super operator

$$\hat{\mathfrak{G}} = \sum_j |\hat{A}_j\rangle(\hat{A}_j| \quad (13.4)$$

is not the unit operator $\hat{1}$ in Liouville space. According to the definition of the transformation operator into the basis $\{|\hat{A}_j\rangle\}$

$$\hat{\mathfrak{V}} = \left(|\hat{A}_1\rangle, \dots, |\hat{A}_d\rangle \right), \quad \hat{\mathfrak{V}}^\dagger = \begin{pmatrix} (\hat{A}_1| \\ \dots \\ (\hat{A}_d| \end{pmatrix} \quad (13.5)$$

one can rewrite (13.4) as

$$\hat{\mathfrak{G}} = \sum_j |\hat{A}_j\rangle(\hat{A}_j| = \hat{\mathfrak{V}} \hat{\mathfrak{V}}^\dagger. \quad (13.6)$$

Thus, the determinant of $\hat{\mathfrak{G}}$ reads

$$\det \hat{\mathfrak{G}} = \det (\hat{\mathfrak{V}} \hat{\mathfrak{V}}^\dagger) = \det \hat{\mathfrak{V}} \det \hat{\mathfrak{V}}^\dagger. \quad (13.7)$$

All basis operators are linearly independent, $\det \hat{\mathfrak{V}} \neq 0$, and thus $\det \hat{\mathfrak{G}} \neq 0$, too. Therefore the operator $\hat{\mathfrak{G}}$ is invertible and one finds a dual basis $|\hat{A}^j\rangle$ according to

$$|\hat{A}^j\rangle = \hat{\mathfrak{G}}^{-1}|\hat{A}_j\rangle \quad (13.8)$$

with the property

$$\sum_j |\hat{A}^j)(\hat{A}_j| = \sum_j |\hat{A}_j)(\hat{A}^j| = \hat{\mathbf{1}} . \quad (13.9)$$

Finally, one can expand any arbitrary operator \hat{X} in a basis in Liouville space

$$\hat{X} = \sum_j |\hat{A}^j)(\hat{A}_j| \hat{X} = \sum_j \text{Tr}\{\hat{A}_j^\dagger \hat{X}\} \hat{A}^j . \quad (13.10)$$

For a more detailed introduction to super operators we will refer the interested reader to some further literature [18, 108, 146–148]¹.

13.2. Unperturbed System

The complete Liouville operator of the system under consideration reads

$$\hat{\mathcal{L}} = \hat{\mathcal{L}}_S + \hat{\mathcal{L}}_1(T_1, \lambda_1) + \hat{\mathcal{L}}_2(T_2, \lambda_2) . \quad (13.11)$$

Again the first term controls the coherent evolution of the chainlike quantum system defined in Sect. 2.1. The chain is weakly coupled to two heat baths, one at each end of the system, given by the super operators $\hat{\mathcal{L}}_1$ and $\hat{\mathcal{L}}_2$, i.e. dissipators as already used several times. More details about the dissipators are not relevant in the following considerations. Just, the possibility of writing the perturbation of the system according to a super operator acting on the state of the system only, is of importance here.

For the unperturbed system both reservoirs are at the same temperature $T_1 = T_2 = T_E$ according to equal coupling strengths $\lambda_1 = \lambda_2 = \lambda_E$. The whole Liouville-von-Neumann equation of the unperturbed system then yields

$$\frac{\partial}{\partial t} |\hat{\rho}\rangle = \left(\hat{\mathcal{L}}_S + \hat{\mathcal{L}}_1(T_E, \lambda_E) + \hat{\mathcal{L}}_2(T_E, \lambda_E) \right) |\hat{\rho}\rangle = \hat{\mathcal{L}}_0 |\hat{\rho}\rangle . \quad (13.12)$$

Since the two baths have exactly the same temperature we expect the system to settle in a thermal stationary state $\hat{\rho}_0$: This state should support neither a heat current nor temperature gradients – it is a global equilibrium state with temperature T_E (see Sect. 4.1).

¹Unfortunately a very interesting work introducing super operator algebra by Tarasov [146] (*Вейлевское квантование динамических систем с плоским фазовым пространством*) is available in Russian language only, some of the discussed aspects could be found in several publications by Tarasov [147, 148] in English. The paper of Mukamel [108] contains interesting operator identities for super operators.

The eigenvalues and eigenvectors of the unperturbed system are given by the eigenequation

$$\hat{\mathfrak{L}}_0|\hat{\rho}_j\rangle = l_j|\hat{\rho}_j\rangle, \quad j = 0, \dots, n^{2N} - 1. \quad (13.13)$$

The unique stationary state $\hat{\rho}_0$ is also an eigenvector of the system with eigenvalue zero, $\hat{\mathfrak{L}}_0|\hat{\rho}_0\rangle = 0$ ($l_0 = 0$, cf. Sect. 4.1), whereas all other eigenvalues have a negative real part. This is due to the fact that the system should enter the equilibrium state $|\hat{\rho}_0\rangle$ asymptotically, regardless of which state the system was at the beginning. Not a single other eigenvector is able to contribute to the equilibrium state, i.e. all other eigenvectors must be unstable.

Based on the fact that all eigenstates form a complete basis for the Liouville space, we can expand each state of the system according to (13.10) in terms of the eigensystem

$$|\hat{\rho}\rangle = \sum_{j=0}^{d-1} |\hat{\rho}_j\rangle (\hat{\rho}^j|\hat{\rho}) = |\hat{\rho}_0\rangle + \sum_{j=1}^{d-1} c_j |\hat{\rho}_j\rangle, \quad (13.14)$$

with the dimension of the Liouville space d (in case of N n -level systems $d = n^{2N}$) and the expansion coefficient $c_j = (\hat{\rho}^j|\hat{\rho})$. Since we have to require that the state $|\hat{\rho}\rangle$ of the system remains normalized for the whole time evolution, each eigenstate must be trace free except $|\hat{\rho}_0\rangle$, which directly follows from the above equation.

13.3. Local Equilibrium State

The system is now perturbed by applying a small temperature gradient ΔT . We start at time $t = -\infty$ and switch on the perturbation exponentially till $t = 0$, letting ΔT constant for all times $t > 0$. Thereafter the system is subject to this small constant external temperature gradient. We are interested in the properties of the stationary *local* equilibrium state of the system reached in the limit $t \rightarrow \infty$. Thus, this state contains stationary currents and a constant temperature profile.

The Liouville operator of the perturbation is introduced as

$$\hat{\mathfrak{L}}'(\Delta T, t) = \hat{\mathfrak{L}}_1\left(T + \frac{\Delta T}{2}f(t)\right) + \hat{\mathfrak{L}}_2\left(T - \frac{\Delta T}{2}f(t)\right), \quad (13.15)$$

with the switch on function

$$f(t) = \Theta(-t)e^t + \Theta(t), \quad \text{with} \quad \Theta(t) = \begin{cases} 0 & t < 0 \\ 1 & t > 0 \end{cases}. \quad (13.16)$$

The two dissipators are the same as before, but with a time dependent temperature difference.

The time evolution of the whole system under the influence of the perturbation is given by the Liouville-von-Neumann equation

$$\frac{\partial}{\partial t} |\hat{\rho}\rangle = (\hat{\mathcal{L}}_0 + \hat{\mathcal{L}}'(\Delta T, t)) |\hat{\rho}\rangle . \quad (13.17)$$

Starting from a thermal equilibrium state $|\hat{\rho}_0\rangle$ in the past, we assume the time dependent state of the whole system to be

$$|\hat{\rho}(t)\rangle = |\hat{\rho}_0\rangle + |\Delta\hat{\rho}(t)\rangle . \quad (13.18)$$

Introducing this into (13.17), suppressing terms of higher order in the perturbation and observing that $\partial\hat{\rho}_0/\partial t = \hat{\mathcal{L}}_0|\hat{\rho}_0\rangle = 0$, one finds the time evolution equation for $|\Delta\hat{\rho}(t)\rangle$,

$$\frac{\partial}{\partial t} |\Delta\hat{\rho}(t)\rangle - \hat{\mathcal{L}}_0 |\Delta\hat{\rho}(t)\rangle = \hat{\mathcal{L}}'(\Delta T, t) |\hat{\rho}_0\rangle . \quad (13.19)$$

We use an operator transformation in Liouville space similar to one in Hilbert space introduced by Kubo (cf. [82])

$$e^{\hat{\mathcal{L}}_0 t} \left(\frac{\partial}{\partial t} \left[e^{-\hat{\mathcal{L}}_0 t} |\Delta\hat{\rho}(t)\rangle \right] \right) = \frac{\partial}{\partial t} |\Delta\hat{\rho}(t)\rangle - \hat{\mathcal{L}}_0 |\Delta\hat{\rho}(t)\rangle . \quad (13.20)$$

This identity is simply shown by differentiating the left hand side of the equation. Using the identity (13.20) in (13.19) one finds

$$\frac{\partial}{\partial t} \left[e^{-\hat{\mathcal{L}}_0 t} |\Delta\hat{\rho}(t)\rangle \right] = e^{-\hat{\mathcal{L}}_0 t} \hat{\mathcal{L}}'(\Delta T, t) |\hat{\rho}_0\rangle . \quad (13.21)$$

Formally integrating this differential equation, one finds the formal solution for the time-dependent perturbation

$$|\Delta\hat{\rho}(t)\rangle = \int_{-\infty}^t dt' e^{\hat{\mathcal{L}}_0(t-t')} \hat{\mathcal{L}}'(\Delta T, t') |\hat{\rho}_0\rangle . \quad (13.22)$$

Thus, the full *local equilibrium state* of the system reads

$$|\hat{\rho}_{\text{leq}}\rangle = |\hat{\rho}_0\rangle + \lim_{t \rightarrow \infty} \int_{-\infty}^t dt' e^{\hat{\mathcal{L}}_0(t-t')} \hat{\mathcal{L}}'(\Delta T, t') |\hat{\rho}_0\rangle . \quad (13.23)$$

13.4. Standard Kubo-Formula

With some preconditions for the unperturbed system and the perturbation one could derive the standard Kubo-formula from (13.22). The mentioned case appears for a Liouville-von-Neumann equation of special kind, reading

$$\frac{\partial \hat{\rho}}{\partial t} = (\hat{\mathcal{L}}_0 + \hat{\mathcal{L}}')|\hat{\rho}) = -\frac{i}{\hbar}[\hat{H}_S + \hat{H}'_t, \hat{\rho}] , \quad (13.24)$$

where, obviously, the perturbation is just a potential part \hat{H}'_t in the complete Hamiltonian, i.e.

$$\hat{\mathcal{L}}'|\hat{\rho}) = -\frac{i}{\hbar}[\hat{H}'_t, \hat{\rho}] . \quad (13.25)$$

Here, we allow for explicitly time-dependent perturbations

$$\hat{H}'_t = F(t)\hat{H}' \quad (13.26)$$

with an explicitly time-independent operator \hat{H}' and an external field $F(t)$, containing switch on functions like (13.16) as well as some oscillating terms with frequency ω . Note that also the unperturbed system does not contain any thermal reservoir any longer.

Consequently, one gets a much simpler form of the time evolution operator² (cf. (2.17)) determining the time evolution of the unperturbed system

$$e^{\hat{\mathcal{L}}_0(t-t')}|\hat{X}) = e^{-\frac{i}{\hbar}\hat{H}_S(t-t')} \hat{X} e^{\frac{i}{\hbar}\hat{H}_S(t-t')} . \quad (13.27)$$

Using these insights in (13.22), one finds

$$|\Delta\hat{\rho}(t)) = -\frac{i}{\hbar} \int_{-\infty}^t dt' e^{-\frac{i}{\hbar}\hat{H}_S(t-t')} [\hat{H}'_t, \hat{\rho}_0] e^{\frac{i}{\hbar}\hat{H}_S(t-t')} . \quad (13.28)$$

Since we guess that $\hat{\rho}_0$ is a thermal equilibrium state of the system finding $\hat{\rho}_0 = \exp(-\beta\hat{H}_S)/Z$, we take the unitary time-evolution operator of the system into the commutator. According to the definition of a time dependent operator in the Heisenberg picture (cf. (3.4))

$$\hat{H}'(t'-t) = e^{\frac{i}{\hbar}\hat{H}_S(t'-t)} \hat{H}' e^{-\frac{i}{\hbar}\hat{H}_S(t'-t)} , \quad (13.29)$$

²Simply shown by using the operator identity

$$e^{\hat{A}} B e^{-\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} [\hat{A}, \hat{B}]_n$$

$$\text{with } [\hat{A}, \hat{B}]_0 := \hat{B} , \quad [\hat{A}, \hat{B}]_1 := [\hat{A}, \hat{B}] , \quad [\hat{A}, \hat{B}]_2 := [\hat{A}, [\hat{A}, \hat{B}]] , \text{ etc.}$$

we finally get

$$|\Delta\hat{\rho}(t)) = -\frac{i}{\hbar} \int_{-\infty}^t dt' F(t') [\hat{H}'(t' - t), \hat{\rho}_0] . \quad (13.30)$$

However, a rather critical point of these considerations is to assume the stationary state $\hat{\rho}_0$ being a thermal equilibrium state, since the unperturbed equation does not contain heat baths any longer. Thus, there is nothing which drives the system to equilibrium or even “near” to equilibrium. Thinking, e.g. of a low dimensional quantum mechanical system, we do not expect a stationary state at all. The state of the system for large times is a strongly coherent fluctuating state, no equilibrium is reached. Of course, there are strong indications that a large system consisting of identical subunits equilibrates itself (see [40, 71]). But for small quantum systems this approximation seems to be rather questionable.

The interesting quantity in context of nonequilibrium states is the current as discussed in Sect. 11.1. Therefore, we investigate the time-dependent state $\hat{\rho}(t) = \hat{\rho}_0 + \Delta\hat{\rho}(t)$ of the system:

$$J = \text{Tr}\{\hat{J}\hat{\rho}(t)\} = \text{Tr}\{\hat{J}\hat{\rho}_0\} + \text{Tr}\{\hat{J}\Delta\hat{\rho}(t)\} = \text{Tr}\{\hat{J}\Delta\hat{\rho}(t)\} . \quad (13.31)$$

Note that a proper equilibrium state $\hat{\rho}_0$ does not contain any currents. Plugging in (13.30) we find

$$J = -\frac{i}{\hbar} \int_{-\infty}^t dt' F(t') \text{Tr}\{\hat{J}[\hat{H}'(t' - t), \hat{\rho}_0]\} . \quad (13.32)$$

Substituting the variable t' of the integration by $x = t - t'$ one finds

$$J = -\frac{i}{\hbar} \int_0^\infty dt' F(t' - t) \text{Tr}\{\hat{J}[\hat{H}'(-t'), \hat{\rho}_0]\} , \quad (13.33)$$

where we have immediately replaced the variable x by t' again (see [96]).

Following Kubo [81], it is convenient to use the celebrated operator identity called *Kubo identity*³

$$[\hat{A}, e^{-\beta\hat{B}}] = -e^{-\beta\hat{B}} \int_0^\beta d\beta' e^{\beta'\hat{B}} [\hat{A}, \hat{B}] e^{-\beta'\hat{B}} , \quad (13.34)$$

³This Kubo identity could be shown by starting from $[\hat{A}, e^{-\beta\hat{B}}] = \exp(-\beta\hat{B})S(\beta)$ with an arbitrary operator function $S(\beta)$. Differentiating this equation with respect to β one finds $\partial S/\partial\beta = -\exp(\beta\hat{B})[\hat{A}, \hat{B}]\exp(-\beta\hat{B})$. By integrating this result over β one gets $S(\beta)$ and thus the above identity (cf. [159]).

valid for any operators \hat{A} and \hat{B} . Thus we may rewrite the commutator of (13.33)

$$J = \frac{i}{\hbar} \int_0^\infty dt' F(t' - t) \int_0^\beta d\beta' \text{Tr}\{\hat{J} \hat{\rho}_0 e^{\beta' \hat{H}_S} [\hat{H}'(-t'), \hat{H}_S] e^{-\beta' \hat{H}_S}\} . \quad (13.35)$$

Since $\hat{H}'(t)$ is an explicitly time-independent operator in the Heisenberg picture its time dependence is controlled by the Heisenberg equation of motion (note $\partial \hat{H}' / \partial t = 0$)

$$\frac{d}{dt} \hat{H}'(t) = \frac{i}{\hbar} [\hat{H}'(t), \hat{H}_S] . \quad (13.36)$$

Using the continuity equation as already done in Sect. 11.1, the time derivative of the perturbation operator is just the current in the system $\hat{J}(t) = d\hat{H}'(t)/dt$ (see, e.g. [82]). In case of a defined external perturbation potential, e.g. oscillating electric or magnetic fields (see [96]), one may furthermore identify the current by $\hat{J}(t) = \frac{i}{\hbar} [\hat{H}'(t), \hat{H}_S]$ following (13.36). In all cases where the current is in fact given by the change of the perturbation in time we thus find (carefully replacing t by $-t'$ in (13.36) and in the current)

$$J = \int_0^\infty dt' F(t' - t) \int_0^\beta d\beta' \text{Tr}\{\hat{J}(-t' - i\hbar\beta') \hat{J} \hat{\rho}_0\} , \quad (13.37)$$

where we again used the transformation into the Heisenberg picture, here according to a “complex time” $i\hbar\beta'$. Basically, this is a current-current autocorrelation function called the *Kubo-formula* for the linear response of a quantum system to an external perturbation.

For an electro magnetic perturbation the external field is just given as a time dependent potential

$$F(t' - t) = F e^{i\omega t'} , \quad \text{with} \quad F = \text{const.} , \quad (13.38)$$

in the Hamiltonian of the system. From linear response (see Sect. 10.4) we know that the current is just proportional to the external force

$$J = \sigma(\omega) F . \quad (13.39)$$

Plugging (13.38) into (13.37), comparing the result to (13.39) one could extract the frequency dependent electric conductivity as

$$\sigma(\omega) = \int_0^\infty dt e^{i\omega t} \int_0^\beta d\beta' \text{Tr}\{\hat{J}(-t - i\hbar\beta') \hat{J} \hat{\rho}_0\} , \quad (13.40)$$

which is exactly what we have introduced in (10.23).

13.5. Kubo-Formula in Liouville Space

For all perturbations described as a potential part in the Hamiltonian of the system the standard Kubo formula is a powerful method to account for any kind of transport coefficient, e.g. susceptibility or electrical conductivity. Unfortunately, the method is not easily extensible to perturbation due to external thermal gradients. Such a perturbation is defined in the Liouville space rather than in the Hilbert space and it is not possible to simply write it down as a potential part of the Hamiltonian. Therefore we switch back to Sect. 13.3 for a perturbation theory in Liouville space, starting from (13.22).

Before we can evaluate (13.22) concretely, we have to concentrate on the dissipators $\hat{\mathfrak{L}}_i$ ($i = 1, 2$), again. Thinking for the moment of the dissipator (3.33) as a super operator acting on the subunits at the edges of the system only, we may proceed as follows: In case of finite reservoir temperatures and two level subunits, the dissipator mainly consists of two transition processes: a decay from the excited level to the ground state of the system and an excitation process, thus reading

$$\hat{\mathfrak{L}}_i(T) = W_i^\downarrow(T)\hat{\mathfrak{E}}_i^\downarrow + W_i^\uparrow(T)\hat{\mathfrak{E}}_i^\uparrow, \quad (13.41)$$

with the rates $W_i^\downarrow(T) = (1 - T)\lambda_E$, $W_i^\uparrow(T) = T\lambda_E$ depending on λ_E being the coupling strength of the respective reservoir and T its temperature. The operators $\hat{\mathfrak{E}}_i^\downarrow$ and $\hat{\mathfrak{E}}_i^\uparrow$ are transition operators. Obviously, this could easily be generalized to an arbitrary number of levels in the system, getting a sum over upward and downward processes for each damping transition. Since in our case the perturbation refers to dissipators at the edges of the system only, we may rewrite the super operator (13.15), accordingly as

$$\hat{\mathfrak{L}}'(\Delta T, t) = \hat{\mathfrak{L}}_1(T) + \hat{\mathfrak{L}}_2(T) + \frac{\Delta T \lambda_E}{2} f(t) \hat{\mathfrak{E}}. \quad (13.42)$$

Thus, the perturbation consists again of super operators defining reservoirs at the same temperature. The interesting term is the second one, since it contains the new time independent perturbation operator $\hat{\mathfrak{E}}$ with some time dependent prefactors. In the simplest case of a chain of two level systems, the special transition operator in terms of the above defined operators (13.41) just reads

$$\hat{\mathfrak{E}} = -\hat{\mathfrak{E}}_1^\downarrow + \hat{\mathfrak{E}}_1^\uparrow + \hat{\mathfrak{E}}_2^\downarrow - \hat{\mathfrak{E}}_2^\uparrow. \quad (13.43)$$

For more energy levels of the subunits in the chain or dissipators acting on the whole system like, e.g. (3.34), one has to account for all possible transitions in

the above described way. This is a complicated, but straight-forward extension to the above considerations, in order to separate the perturbation operator into a time independent reservoir operator with equal temperatures and a time dependent perturbation.

The first two terms of (13.42) just replicate the bath operators with the same temperature at both ends. Acting on the unperturbed equilibrium state these terms vanish and therefore (13.22) reduces to

$$|\Delta\hat{\rho}(t)\rangle = \frac{\Delta T \lambda_E}{2} \int_{-\infty}^t dt' e^{\hat{\mathcal{E}}_0(t-t')} f(t') \hat{\mathfrak{E}} |\hat{\rho}_0\rangle. \quad (13.44)$$

According to the complete basis of the eigenstates of the unperturbed system, this equation could be further simplified. Introducing the unit operator (13.9) due to the eigenbasis of the unperturbed system into (13.44) yields

$$|\Delta\hat{\rho}(t)\rangle = \frac{\Delta T \lambda_E}{2} \int_{-\infty}^t dt' e^{\hat{\mathcal{E}}_0(t-t')} \sum_j |\hat{\rho}_j\rangle (\hat{\rho}^j | f(t') \hat{\mathfrak{E}} |\hat{\rho}_0\rangle). \quad (13.45)$$

Using the eigensystem of the unperturbed model and especially $e^{\hat{\mathcal{E}}_0(t-t')} |\hat{\rho}_j\rangle = e^{l_j(t-t')} |\hat{\rho}_j\rangle$ we find

$$|\Delta\hat{\rho}(t)\rangle = \frac{\Delta T \lambda_E}{2} \sum_j (\hat{\rho}^j | \hat{\mathfrak{E}} |\hat{\rho}_0\rangle) |\hat{\rho}_j\rangle \int_{-\infty}^t e^{l_j(t-t')} f(t') dt'. \quad (13.46)$$

By integrating over t' with the function $f(t')$ as defined in (13.16) and observing that the real part of l_j is negative (for $j \neq 0$), we finally get the time dependent perturbation of the density operator

$$\begin{aligned} |\Delta\hat{\rho}(t)\rangle &= \frac{\Delta T \lambda_E}{2} \left[(1+t)(\hat{\rho}^0 | \hat{\mathfrak{E}} |\hat{\rho}_0\rangle) |\hat{\rho}_0\rangle \right. \\ &\quad \left. + \sum_{j=1}^{d-1} \left(\frac{e^{l_j t}}{1-l_j} + \frac{e^{l_j t}-1}{l_j} \right) (\hat{\rho}^j | \hat{\mathfrak{E}} |\hat{\rho}_0\rangle) |\hat{\rho}_j\rangle \right]. \end{aligned} \quad (13.47)$$

The first term results from the integration over the addend $j = 0$, the sum contains the rest. Rewriting the matrix element of the super operator $\hat{\mathfrak{E}}$ as a scalar product defined by (13.2), we find

$$(\hat{\rho}^0 | \hat{\mathfrak{E}} |\hat{\rho}_0\rangle) = (\hat{\rho}^0 | \hat{\mathfrak{E}} \hat{\rho}_0\rangle) = \text{Tr}\{\hat{\rho}_0(\hat{\mathfrak{E}} \hat{\rho}_0)\}. \quad (13.48)$$

The conservation of the trace of the complete Liouville-von-Neumann equation requires that each operator produced by an action of the perturbation operator

$\hat{\mathfrak{E}}$ on an arbitrary density operator has to be a trace free operator. Since $|\hat{\rho}_0\rangle$ is the only basis state with non-zero trace, as argued before (see 13.2), we have to require that $\hat{\mathfrak{E}}|\hat{\rho}_0\rangle$ does not have a component in $|\hat{\rho}_0\rangle$ direction. Therefore this matrix element should be zero and (13.47) reduces to

$$|\Delta\hat{\rho}(t)\rangle = \frac{\Delta T \lambda_E}{2} \sum_{j=1}^{d-1} \left(\frac{e^{l_j t}}{1 - l_j} + \frac{e^{l_j t} - 1}{l_j} \right) (\hat{\rho}^j | \hat{\mathfrak{E}} | \hat{\rho}_0) |\hat{\rho}_j\rangle. \quad (13.49)$$

This perturbative term will include all currents and local temperature gradients of the system under the given perturbation.

Since we are interested in a local equilibrium state – a stationary state with a constant current and temperature profile, which will be reached after a certain relaxation time – we consider (13.49) in the limit of $t \rightarrow \infty$ finding

$$|\Delta\hat{\rho}\rangle = \lim_{t \rightarrow \infty} |\Delta\hat{\rho}(t)\rangle = -\frac{\Delta T \lambda_E}{2} \sum_{j=1}^{d-1} \frac{(\hat{\rho}^j | \hat{\mathfrak{E}} | \hat{\rho}_0)}{l_j} |\hat{\rho}_j\rangle. \quad (13.50)$$

This is the first-order change of the density operator introduced by the perturbation. Let us call this equation the Kubo-formula in Liouville space (see also [82]). Note the similarity with the Hilbert space perturbation: the change of the density operator due to the perturbation then depends on both the matrix element of the perturbation operator and all eigenstates of the unperturbed system (see also Sect. 14.1).

13.6. Heat Transport Coefficient

Now we are prepared to account in such Kubo-Liouville scenarios for the local temperature profile and the expectation value of the current. The respective operators for the investigation of such nonequilibrium steady states are defined in Chap. 11.

The whole stationary density operator of the system is given by $|\hat{\rho}\rangle = |\hat{\rho}_0\rangle + |\Delta\hat{\rho}\rangle$. Since we know that $|\hat{\rho}_0\rangle$ does not contribute to any local temperature difference or heat current, the expectation value of the operators is determined by $|\Delta\hat{\rho}\rangle$ only. Therefore we find for the local internal temperature gradient

$$\begin{aligned} \delta T(\mu, \mu + 1) &= \text{Tr}\{\Delta\hat{H}_{\text{loc}}(\mu, \mu + 1)\Delta\hat{\rho}\} \\ &= -\frac{\Delta T \lambda_E}{2} \sum_{j=1}^{d-1} \frac{(\hat{\rho}^j | \hat{\mathfrak{E}} | \hat{\rho}_0)}{l_j} \text{Tr}\{\Delta\hat{H}_{\text{loc}}(\mu, \mu + 1)\hat{\rho}_j\} \end{aligned} \quad (13.51)$$

and the local current within the system

$$\begin{aligned} J(\mu, \mu + 1) &= \text{Tr}\{\hat{J}(\mu, \mu + 1)\Delta\hat{\rho}\} \\ &= -\frac{\Delta T \lambda_E}{2} \sum_{j=1}^{d-1} \frac{(\hat{\rho}^j | \hat{\mathfrak{E}} | \hat{\rho}_0)}{l_j} \text{Tr}\{\hat{J}(\mu, \mu + 1)\hat{\rho}_j\}. \end{aligned} \quad (13.52)$$

The current as well as the local temperature gradient are thus found to linearly depend on the global temperature difference of the bath systems. Under stationary conditions the current must be independent of μ , $J(\mu, \mu + 1) = J$, so that (13.52) can be rewritten as

$$J = -\kappa' \Delta T, \quad (13.53)$$

defining the so-called *global conductivity* as

$$\kappa' = \frac{\lambda_E}{2} \sum_{j=1}^{d-1} \frac{(\hat{\rho}^j | \hat{\mathfrak{E}} | \hat{\rho}_0)}{l_j} \text{Tr}\{\hat{J}(\mu, \mu + 1)\hat{\rho}_j\}. \quad (13.54)$$

Eigenstates and eigenvalues entering this global conductivity κ' only depend on the mean temperature of the unperturbed system not on ΔT (cf. Sect. 10.1, especially (10.7)). Based on this κ' as a global property of the system, including its contact properties, we call (13.53) *external Fourier's Law*. Therein the global conductivity (13.54) defines the overall resistance of our given quantum system.

Furthermore, combining (13.51) and (13.52), we can define a *local conductivity* within the system

$$\kappa(\mu, \mu + 1) = -\frac{J(\mu, \mu + 1)}{\delta T(\mu, \mu + 1)} = -\frac{J}{\delta T(\mu, \mu + 1)} \quad (13.55)$$

implying $\kappa(\mu, \mu + 1)$ to be independent of the external difference ΔT .

The most remarkable point of the above result for the heat current and the temperature profile is the fact that the global temperature difference of the external bath systems shows up only as a parameter. Thus, the heat conductivity is independent of the external gradient ΔT , and the *external Fourier's Law* is always fulfilled, even if the internal gradient of the system is anything but linear, as long as the perturbation theory applies.

The presented approach does not have the problem of introducing a potential term into the Hamiltonian of the system, like in standard Kubo formulas for heat conduction. The bath systems, modeled by a quantum master equation, directly define the perturbation in Liouville space. Like in standard perturbation theory in Hilbert space the first order correction to the stationary

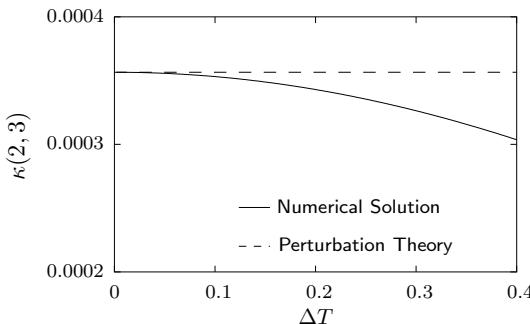


Figure 13.1.: Local conductivity $\kappa(2,3)$ in a Heisenberg spin chain of 4 spins as a function of the external perturbation ΔT ; the solid line refers to the solution of the full Liouville-von-Neumann equation, the dashed line shows the result of the perturbation theory.

state of the system is expressed in terms of transition matrix elements of the perturbation operator and the eigenstates and eigenvalues of the unperturbed system. Only the non-orthogonality of the eigensystem of the unperturbed Liouvillian needs a more careful treatment, formally the equations are very similar.

13.7. Heat Conductivity of a Model System

We now compare the result according to the perturbation theory with the full numerical solution of the Liouville-von-Neumann equation, here for a Heisenberg spin chain with four spins. In Fig. 13.1 we show the local conductivity of the two central spin systems $\kappa(2,3)$ as a function of the external gradient ΔT . Indeed, we find numerically that $\kappa(2,3)$ according to (13.55) does not depend on ΔT (dashed line). The exact numerical solution of the Liouville-von-Neumann equation shows a weak ΔT dependence (solid line). As expected, linear transport and our perturbational theory applies for not too large external gradients ΔT only. Note that the full range of temperatures $0 \leq T < \infty$ has been mapped here onto the interval $[0, 0.5]$; $\Delta T = 0.3$ is thus already a very large difference.

The theoretical predictions of our perturbation theory concerning temperature gradients and currents within the chain for all investigated systems (Heisenberg, XY and random coupling model) are in very good accordance with the numerical solution of the complete Liouville-von-Neumann equation

of the system (compare [102, 105]).

Normal heat conduction is associated with a constant but non-zero local temperature gradient and thus a finite conductivity $\kappa(\mu, \mu + 1) = \kappa$ independent of site μ (see [40, 96]). The majority of coupling types within the chain, the Heisenberg coupling and the random next neighbor interaction indeed show this normal behavior in the weak coupling limit [40, 105]. But this normal transport type does not appear for the energy transfer coupling only (XY model). The vanishing gradient in such a coupling scenario implies a divergent conductivity within the chain. Nevertheless, the current remains finite because of the resistance at the contacts, therefore the global conductivity κ defined in (13.54) remains finite for this special coupling type, too. Therefore we can state that the *external Fourier's Law is valid even if Fourier's Law proper does not apply*. These results can be compared with the numerical results of the full solution of the Liouville-von-Neumann equation and we find perfect agreement.

14. Reservoir Perturbation Theory

During the International Congress on Mathematical Physics held in London in the year 2000, J. L. Lebowitz expressed his opinion that one of the great challenges to mathematical physics in the twenty-first century is the theory of heat conductivity and other transport phenomena in macroscopic bodies.

R. Alicki and M. Fanes in [1]

In the preceding Chapter we have investigated the quantum mechanical model of heat conduction in terms of a perturbation theory in Liouville space. Considering the external temperature difference of the reservoirs as a perturbation the system approaches a *local equilibrium state* initially being in a global one. In comparison to the numerical results of previous Chapters the theoretical approach explains the dependencies of the heat conductivity in small quantum systems in a reasonable way.

In the present Chapter we will give a short summary of the new perturbation theory. We will concentrate on the relationship to some standard perturbation techniques. Furthermore, we would like to investigate the dependence of the transport properties, global as well as local ones, on the reservoir coupling strength. Therefore, we introduce yet another perturbation theory with respect to this external parameter. As a bulk property, the local heat conductivity far away from the reservoirs should not depend on the heat bath coupling strength. However, since we have already discussed the limitation of the heat current according to the reservoir contacts, such an investigation should only be successful for large systems.

14.1. Perturbation Theory

In the most general case we could investigate the following Liouvillian

$$\hat{\mathfrak{L}} = \hat{\mathfrak{L}}_0 + \alpha \hat{\mathfrak{L}}' \quad (14.1)$$

with the unperturbed part $\hat{\mathcal{L}}_0$ and a perturbation operator $\hat{\mathcal{L}}'$ according to some kind of smallness parameter α . The stationary state of the unperturbed system is given by $|\hat{\rho}_0^{(0)}\rangle$, a real *thermal state*. The full eigensystem reads

$$\hat{\mathcal{L}}_0|\hat{\rho}_i^{(0)}\rangle = l_i^{(0)}|\hat{\rho}_i^{(0)}\rangle \quad (14.2)$$

with $l_0^{(0)} = 0$.

As usually done, the eigensystem of the perturbed system can be expanded in powers of the parameter α finding

$$l_i = l_i^{(0)} + \alpha l_i^{(1)} + \cdots, \quad |\hat{\rho}_i\rangle = |\hat{\rho}_i^{(0)}\rangle + \alpha |\hat{\rho}_i^{(1)}\rangle + \cdots. \quad (14.3)$$

Now, we closely follow ideas of the standard Hilbert space perturbation theory as used in many text books. Plugging the above expansion into the eigenequation of the whole system, solving for each order in α separately, one finds the perturbed eigenvalues

$$l_i^{(1)} = (\hat{\rho}_{(0)}^i | \hat{\mathcal{L}}' | \hat{\rho}_i^{(0)}) . \quad (14.4)$$

Note, however, that one needs the dual basis $|\hat{\rho}_{(0)}^i\rangle$, here. This is due to the fact that the unperturbed eigensystem is not necessarily orthogonal as discussed before (see Sect. 13.1). By a straight forward computation like in the Hilbert space one finds from this perturbed eigenvalue the first order perturbed eigenstate as

$$|\hat{\rho}_i^{(1)}\rangle = \sum_j \frac{(\hat{\rho}_{(0)}^j | \hat{\mathcal{L}}' | \hat{\rho}_i^{(0)})}{l_i^{(0)} - l_j^{(0)}} |\hat{\rho}_j^{(0)}\rangle . \quad (14.5)$$

Comparing this first order deviation for the stationary state $i = 0$, remembering that $l_0^{(0)} = 0$, with the former result (13.50), we exactly find the same formula. Thus, the new Liouville space perturbation theory is quite similar to the standard Hilbert space perturbation theory except for the usage of the dual basis.

14.2. Dependence on the Bath Coupling

In the following, we discuss the dependence of the heat conductivity, the heat current and the local temperature gradient on the reservoir coupling strength. In order to investigate those dependencies we solve the Liouville-von-Neumann equation for a model consisting of $N = 4$ spins with local energy splitting $\Delta E = 1$ and a Heisenberg interaction with coupling strength

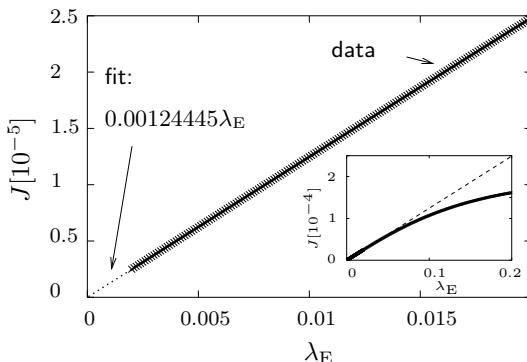


Figure 14.1.: Dependence of the current on the external coupling strength λ_E . Crosses refer to numerical data, dashed line to a fit. The inset shows a larger scale.

$\lambda = 0.1$. This system is coupled to two heat baths according to the dissipator (3.33) with the mean temperature $T = 0.2$ and the temperature difference $\Delta T = 0.01$ (cf. 12.1) as done before. Again, all temperatures are measured in units of the local energy splitting ΔE here. We change the coupling strength $\lambda_1 = \lambda_2 = \lambda_E$ of the two bath systems in the interval $[0.002, 0.2]$. After a numerical computation of the stationary local equilibrium state of the system, we account for the current, the temperature gradient and the heat conductivity in the center of the system.

The dependence of the current on the reservoir coupling λ_E is depicted in Fig. 14.1. It turns out that the current is a linear function of the external coupling strength at least for small λ_E (cf. inset of Fig. 14.1). This does not come as a complete surprise, since the current itself essentially is a result of the coupling between system and the reservoirs. Thus, it should increase for an improved contact to the environment.

Besides the increasing current, the temperature difference also increases with the external coupling strength, shown in Fig. 14.2. The gradient shows a quadratic behavior for small λ_E . However, for large values it levels off (cf. inset of Fig. 14.2). Thus, we find the local temperature in the centre of the system to depend on the coupling parameter to the environment. This seems to be a strange result, since “far away” from the reservoirs the local temperature gradient should only depend on material properties of the system.

Finally the above described results lead to a dependence of the heat conductivity inside the system on the coupling strength of the bath systems, as shown in Fig. 14.3. At least for small external coupling strengths, the conduc-

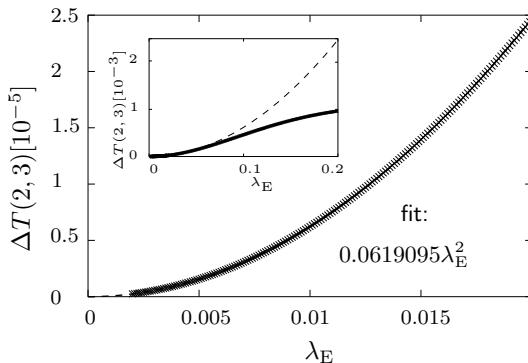


Figure 14.2.: Dependence of internal temperature gradient on the external coupling strength λ_E . Crosses refer to numerical data, dashed line to a fit. The inset shows a larger scale.

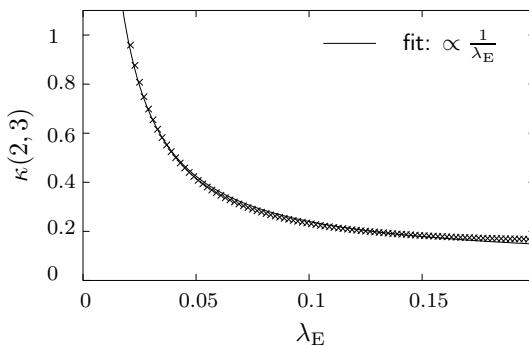


Figure 14.3.: Dependence of the heat conductivity on the bath coupling λ_E . Crosses refer to numerical data. Data is fitted according to $1/\lambda_E$.

tivity should decrease proportionally to λ_E^{-1} , according to the above results of current and temperature gradient.

As a bulk property we would have expected to find the heat conductivity to be independent of the external parameter λ_E . However, this may only be the case far away from the contacts. Since the considered system is really small, containing four spins only, it will possibly never be feasible to observe the respective behavior, here. Furthermore, according to the increasing numerical effort it is hard to investigate larger systems. Thus, it may hardly be possible to get to the limit of being “far away” from any reservoir. In the following we consider these properties in more detail by a perturbation theory. Such an approach might shed new light on the problem.

14.3. Influence of the Bath Coupling

We consider the Liouvillian

$$\hat{\mathcal{L}} = \hat{\mathcal{L}}_S + \hat{\mathcal{L}}_1(T_1, \lambda_1) + \hat{\mathcal{L}}_2(T_2, \lambda_2), \quad (14.6)$$

containing a coherent part $\hat{\mathcal{L}}_S$ and two incoherent dissipators. We use the special perturbation operator introduced in Sect. 13.5, especially (13.41), here. Thus, for a chain of two level systems coupled to two dissipators as introduced in (3.33), the perturbation super operator essentially consists of two transition processes

$$\hat{\mathcal{L}}_i(T_i, \lambda_i) = W_i^\downarrow(T_i, \lambda_i)\hat{\mathfrak{E}}_i^\downarrow + W_i^\uparrow(T_i, \lambda_i)\hat{\mathfrak{E}}_i^\uparrow. \quad (14.7)$$

The rates W_i^\downarrow , W_i^\uparrow are functions of the bath parameters, temperature and coupling strength. Let the temperatures be $T_{1/2} = T \pm \Delta T/2$ as before. Choosing the reservoir coupling strength as $\lambda_1 = \lambda_2 = \lambda_E + \Delta\lambda$ the rates yield

$$W_{1/2}^\downarrow = (1 - T \mp \Delta T)(\lambda_E + \Delta\lambda), \quad (14.8)$$

$$W_{1/2}^\uparrow = (T \pm \Delta T)(\lambda_E + \Delta\lambda). \quad (14.9)$$

Plugging these rates into the Liouvillian (14.6) we get

$$\begin{aligned} \hat{\mathcal{L}} = & \hat{\mathcal{L}}_S + \hat{\mathcal{L}}_1(T, \lambda_E) + \hat{\mathcal{L}}_2(T, \lambda_E) \\ & + \Delta\lambda(\hat{\mathcal{L}}_1(T, 1) + \hat{\mathcal{L}}_2(T, 1)) + (\lambda_E\Delta T + \Delta\lambda\Delta T)\hat{\mathfrak{E}}, \end{aligned} \quad (14.10)$$

with the special perturbation operator $\hat{\mathfrak{E}} = -\hat{\mathfrak{E}}_1^\downarrow + \hat{\mathfrak{E}}_1^\uparrow + \hat{\mathfrak{E}}_2^\downarrow - \hat{\mathfrak{E}}_2^\uparrow$, cf. (13.43). Again, the Liouvillian of the unperturbed system reads $\hat{\mathcal{L}}_0 = \hat{\mathcal{L}}_S + \hat{\mathcal{L}}_1(T, \lambda_E) +$

$\hat{\mathfrak{L}}_2(T, \lambda_E)$, with equal temperatures and coupling strengths for both reservoirs. Thus, the rest of (14.10) defines the perturbation super operator

$$\hat{\mathfrak{L}}' = \Delta\lambda \left(\hat{\mathfrak{L}}_1(T, 1) + \hat{\mathfrak{L}}_2(T, 1) \right) + (\lambda_E \Delta T + \Delta\lambda \Delta T) \hat{\mathfrak{E}}. \quad (14.11)$$

The first term of this operator is just proportional to the super operator of the two bath systems at the same temperature, but with a different coupling strength. The perturbation of the equilibrium state is given by (13.22). Therein, the perturbation operator directly acts on the unperturbed equilibrium state. The application of an operator, proportional to both baths at the same equilibrium temperature T , to the equilibrium density operator is zero irrespective of how strong the environment is coupled to the system (cf. Sect. 13.5). Therefore, this term does not contribute to the local equilibrium state.

The second operator contains two different terms. The first one which is proportional to $\lambda_E \Delta T$ is just the same as in the perturbation theory of the last Chapter. The second one is to some extent the first perturbation term according to the external coupling parameter change $\Delta\lambda$. This lowest order term is also associated with the same super operator $\hat{\mathfrak{E}}$. Therefore, we could simply replace all parameters $\lambda_E \Delta T$ by $(\lambda_E \Delta T + \Delta\lambda \Delta T)$ in the last Chapter. This results in a conductivity κ independent of the new parameters, like in Chap. 13 where the heat conductivity does not depend on the external temperature gradient. However, we know from Sect. 14.2 that the conductivity in these small systems depends on the external coupling strength of the bath system (see again Fig. 14.2). Therefore, the first order perturbation theory appears to fail here.

We again consider the last term of (14.11) proportional to $\Delta\lambda \Delta T$. Since all changes of the density operator according to the perturbation refer to $\hat{\mathfrak{E}}$, this term is the lowest order of the reservoir coupling perturbation theory. However, this term seems to be of *second order in the perturbation* since it is proportional to ΔT , too. It will turn out that this is exactly the problem here.

In the last Chapter we did a perturbation theory in ΔT , treating λ_E as a fixed parameter. Doing the same for $\Delta\lambda$, treating ΔT as being fixed (as also done in the numerical investigation of the last Section) and not as a perturbational “smallness” parameter, theory completely fails. This is a result of the following difference: The correct result of the last Chapter refers to the fact that the first order terms separate in λ_E and T and the leading term of the perturbation theory in the gradient is of first order. The main difference for the perturbation theory in the reservoir coupling strength λ_E is that the leading term is of second order. The first order does not exist. Thus, the

separate perturbation theory in the reservoir coupling is doomed to failure, since it does not separate from the perturbation theory in the gradient in lowest order (second order). Finding the leading term of the reservoir coupling perturbation theory to be of second order, we have to consider several further second order terms to get a proper perturbation theory in the two parameters.

Since a complete second order perturbation theory is very complicated, we only roughly describe how a heat conductivity depending on the reservoir coupling strength could emerge. The above perturbation operator can be written as

$$\hat{\mathcal{L}}' = \mathfrak{a} \hat{\mathfrak{F}} + \mathfrak{b} \hat{\mathfrak{E}}, \quad (14.12)$$

according to the super operator $\hat{\mathfrak{F}} = \hat{\mathcal{L}}_1(T, 1) + \hat{\mathcal{L}}_2(T, 1)$ and the parameters $\mathfrak{a} = \Delta\lambda$ and $\mathfrak{b} = \Delta T(\lambda_E + \Delta\lambda)$. Since the change in the density operator is a function of this perturbation operator we could state that it is also a function of the two parameters \mathfrak{a} and \mathfrak{b} . Thus, also the expectation value $X(\mathfrak{a}, \mathfrak{b})$ of an operator \hat{X} depends on the parameters. A Taylor expansion to second order of this two dimensional function is given by

$$X(\mathfrak{a}, \mathfrak{b}) = X_0 + c_{\mathfrak{a}} \mathfrak{a} + c_{\mathfrak{b}} \mathfrak{b} + c_{\mathfrak{a}\mathfrak{b}} \mathfrak{a}\mathfrak{b} + c_{\mathfrak{aa}} \mathfrak{a}^2 + c_{\mathfrak{bb}} \mathfrak{b}^2, \quad (14.13)$$

where the c 's are some complicated sums over all eigenstates of the unperturbed system, containing expectation values of the respective operator. The expansion of the current and the local gradient reads

$$J(\mathfrak{a}, \mathfrak{b}) = J_0 + c_{\mathfrak{a}} \mathfrak{a} + c_{\mathfrak{b}} \mathfrak{b} + c_{\mathfrak{ab}} \mathfrak{ab} + c_{\mathfrak{aa}} \mathfrak{a}^2 + c_{\mathfrak{bb}} \mathfrak{b}^2, \quad (14.14)$$

$$\delta T(\mathfrak{a}, \mathfrak{b}) = \delta T_0 + \tilde{c}_{\mathfrak{a}} \mathfrak{a} + \tilde{c}_{\mathfrak{b}} \mathfrak{b} + \tilde{c}_{\mathfrak{ab}} \mathfrak{ab} + \tilde{c}_{\mathfrak{aa}} \mathfrak{a}^2 + \tilde{c}_{\mathfrak{bb}} \mathfrak{b}^2. \quad (14.15)$$

According to the fact that the unperturbed system does not contain any currents or gradients we immediately find that the constant terms J_0 and δT_0 vanish. Furthermore, all terms exclusively in \mathfrak{a} vanish, too ($c_{\mathfrak{a}} = \tilde{c}_{\mathfrak{a}} = 0$, etc), as discussed above. Since the term in \mathfrak{b}^2 is basically dependent on $(\Delta T)^2$ (all other terms are of third order) and the leading term of the perturbation in the gradient is already of first order we may neglect this term. The heat conductivity, thus, reads

$$\kappa = \frac{J(\mathfrak{a}, \mathfrak{b})}{\delta T(\mathfrak{a}, \mathfrak{b})} = \frac{c_{\mathfrak{b}} \mathfrak{b} + c_{\mathfrak{ab}} \mathfrak{ab}}{\tilde{c}_{\mathfrak{b}} \mathfrak{b} + \tilde{c}_{\mathfrak{ab}} \mathfrak{ab}}. \quad (14.16)$$

Plugging in the definitions of the parameters \mathfrak{a} and \mathfrak{b} and neglecting third order terms one gets

$$\kappa = \frac{\Delta T \lambda_E c_{\mathfrak{b}} + \Delta T \Delta \lambda (c_{\mathfrak{b}} + \lambda_E c_{\mathfrak{ab}})}{\Delta T \lambda_E \tilde{c}_{\mathfrak{b}} + \Delta T \Delta \lambda (\tilde{c}_{\mathfrak{b}} + \lambda_E \tilde{c}_{\mathfrak{ab}})}. \quad (14.17)$$

From this equation, especially from the last term in the denominator and the numerator, we conclude that κ keeps a non-trivial dependence on the bath coupling strength. This finding is in accordance with the numerical results of the last Section.

In conclusion we find a dependence on the reservoir coupling strength of the heat conductivity. This result may not come as a surprise in such small systems. Especially, the linear dependence of the current on λ_E seems to be understandable, since the quality of the contact is responsible for the current in the system, too. However, as a bulk property we would like to find something independent of the environment. Maybe in future investigations we will be able to show that the dependence of the bath coupling vanishes for larger systems.

In face of all those problems we will present a completely different approach to heat conduction in small quantum systems below.

15. Quantum Thermodynamic Approach to Heat Conduction

Actually, the very definition of local energy flux [...] and of temperature field [...] relies on the *local equilibrium hypothesis* i.e. on the possibility of defining a local temperature for a macroscopically small but microscopically large volume [...].

S. Lepri, R. Livi and A. Politi in [88]

In the previous Chapters we have discussed a new Liouville space perturbation theory showing that the heat conductivity depends explicitly on the reservoir coupling strength. We hope to overcome this deficiency in the future by considering larger chains containing more subunits. However, there are neither theoretical nor numerical investigations of larger systems feasible at the moment.

Thus, we turn to yet another approach to heat transport within quantum mechanics based on the Hilbert Space Average Method (HAM) already used for the investigation of the decay to equilibrium in the first part of the present text (see also [37, 38, 40, 104, 106]). This method allows for a prediction of the Schrödinger evolution of certain “coarse grained” observables, such as, e.g. the occupation probability of a whole energy band. However, in order to apply HAM we need a completely different model scenario. Instead of coupling the system to several reservoirs we observe the decay of the system into the global equilibrium state. Applied to regular chains of many level quantum systems in such a decay scenario, HAM predicts that the energy transfer between two adjacent systems only depends on the energy difference between them.

The idea behind this different approach has already been discussed by Einstein in his considerations on Brownian motion [26, 27]. Therein, Einstein used two completely different approaches to account for the diffusion coefficient of small molecules suspended in a fluid. He considered a dynamical

equilibrium state¹ due to a gradient of concentration first. A diffusion process is present inside the fluid introduced by some external concentration gradients. The Stokes friction with the friction coefficient ξ works against the free motion of the molecules in the fluid. Finally, one finds under this dynamical equilibrium precondition the diffusion coefficient for the particles

$$D = \frac{k_B T}{\xi}, \quad (15.1)$$

sometimes called the Stokes-Einstein relation (see [48]). This relation combines the diffusion constant and therefore the thermodynamical motion of the system with the friction being the response of the system to an external force.

A completely different scenario is the idea of an initial nonequilibrium distribution of the concentration inside the fluid. Due to the Brownian motion of the particles one finds a tendency towards a final equilibrium state with equally distributed particles². This process is described by the diffusion equation

$$\frac{\partial \underline{\varrho}}{\partial t} = D' \frac{\partial^2 \underline{\varrho}}{\partial x^2}, \quad (15.2)$$

where $\underline{\varrho}$ is the position and time dependent density of the particles and D' another diffusion coefficient

$$D' = \frac{\bar{l}^2}{2\tau}, \quad (15.3)$$

where \bar{l} refers to the mean path of a particle in the time interval τ . The idea of Einstein and Smoluchowski [140] was to equate these two diffusion coefficients mainly to state that the process of a relaxation to equilibrium is in principal subject to the same physical property of a system like the dynamical equilibrium state – the diffusion coefficient $D = D'$.

In the following we transfer those ideas to heat transport. As a consequence, the heat conductivity becomes the main physical quantity being responsible for both, the properties of the stationary local equilibrium state as well as the respective decay behavior of the same system.

¹ “In einer Flüssigkeit seien suspendierte Teilchen regellos verteilt. Wir wollen den dynamischen Gleichgewichtszustand derselben untersuchen unter der Voraussetzung, daß auf die einzelnen Teilchen eine Kraft K wirkt, welche vom Ort, nicht aber von der Zeit abhängt.” (Einstein, [26, p. 554])

² “Der unregelmäßige Bewegungsprozeß, als welchen wir den Wärmeinhalt einer Substanz aufzufassen haben, wird bewirken, daß die einzelnen Moleküle einer Flüssigkeit in denkbar unregelmäßigster Weise ihren Ort ändern. Dieses gewissermaßen planlose Umherirren der Moleküle gelöster Substanz in einer Lösung wird zur Folge haben, daß eine anfängliche ungleichmäßige Konzentrationsverteilung der gelösten Substanz allmählich einer gleichmäßigen Platz machen wird.” (Einstein, [27, p. 237])

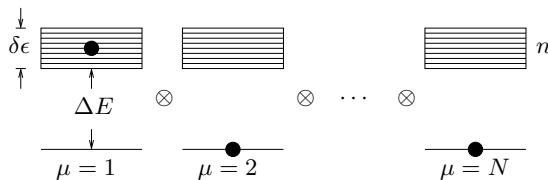


Figure 15.1.: Heat conduction model: N coupled subunits with ground level and band of n equally distributed levels ($\Delta E = 1$). Black dots refer to used initial states.

15.1. Mesoscopic Model

The class of systems we are going to analyze next is depicted in Fig. 15.1, again characterized by the Hamiltonian (2.1). Instead of using two level systems the N identical subunits feature a non-degenerate ground state and a band of n excited states each, equally distributed over some band width $\delta\epsilon$ in such a way that the band width is small compared to the local energy gap ΔE ($\delta\epsilon \ll \Delta E$, $\delta\epsilon$ in units of ΔE). These subunits are coupled by an energy exchanging next neighbor interaction $\hat{H}_{\text{int}}(\mu, \mu + 1)$, chosen to be a (normalized) random Hermitian matrix allowing for any possible transition such as to avoid any bias. Our results will turn out to be independent of the exact form of the matrix. We choose the next neighbor coupling to be weak compared to the local gap ($\lambda \ll \Delta E$, λ in units of ΔE). The “microcanonical” interaction within a single band as discussed in Chap. 9 will not be included. This way the full energy is approximately given by the sum of the local energies and these are approximately given by

$$\langle \psi(t) | \hat{H}_{\text{loc}}(\mu) | \psi(t) \rangle = \Delta E P_\mu \quad (15.4)$$

where P_μ is the probability to find the μ -th subsystem in its excited state.

This system could be seen as a model for an interacting chain of mesoscopic systems each featuring a gapped band structure as already investigated by other methods (cf. [122]). It could be interpreted to result, e.g. from an integer number spin chain which is gapped according to the Haldane-conjecture [50, 132]. Furthermore, the big advantage of the present model is the clear partition of the Hamiltonian in a local respectively interaction part. This partition allows for a unique definition of both a local energy respectively temperature as well as a proper current. Anyway, our model is primarily meant to demonstrate how energy transport might emerge from Schrödinger dynamics – a statistical diffusive behavior from a time reversible microscopic Schrödinger dynamics.

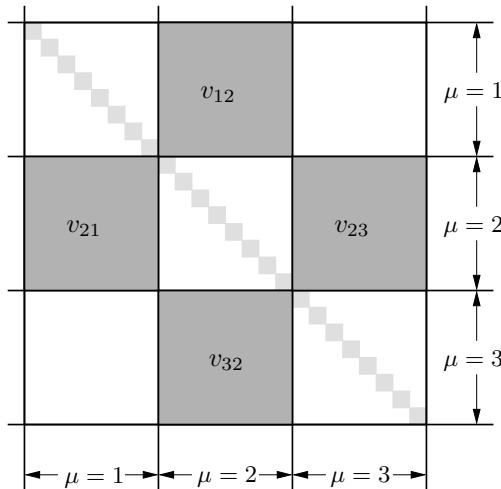


Figure 15.2.: Reduced Hamiltonian (local part light gray, interaction dark gray) of the one excitation subspace in order to investigate heat conduction in the model displayed in Fig. 15.2 ($N = 3$ subunits).

Restricting ourselves to the single excitation subspace, i.e. initial states with one system somewhere in the upper band all others in their ground state, we can derive a reduced Hamiltonian model. The respective Hamiltonian matrix is shown in Fig. 15.2, here for three subsystems only. This matrix could simply be extended to more than three systems by adding such diagonal blocks with the respective off-diagonal interaction. Note that this matrix is similar to the structure of the Hamiltonian in decay scenarios of Chap. 6 and Chap. 8, especially cf. Fig. 8.1. Again we skip all diagonal couplings as well as non energy conserving terms.

As in the consideration of the decay the state vector is divided into several parts: the upper one contains all states belonging to the first subsystem in its upper band all others in the ground state, the next part to all states in the upper level of the second subsystem etc. Like in Chap. 6 we introduce projection operators $\hat{P}_{\mu,\mu}$. These operators are matrices with the unit operator of dimension n at position (μ, μ) and zeros elsewhere. Therefore the operator $\hat{P}_{\mu,\mu}$ projects out the part of the state describing the μ th system being in the upper band. The whole state is thus given by

$$|\psi\rangle = \sum_{\mu} \hat{P}_{\mu,\mu} |\psi\rangle = \sum_{\mu} |\psi_{\mu}\rangle , \quad (15.5)$$

where none of the $|\psi_\mu\rangle$ s is normalized individually. Furthermore, one may also introduce some standard transition operators $\hat{P}_{\mu,\nu}$ with an unit operator at position (μ, ν) . Two properties are important in this context:

$$\hat{P}_{\mu+1,\mu}\hat{P}_{\mu,\mu} = \hat{P}_{\mu+1,\mu+1}\hat{P}_{\mu+1,\mu}, \quad \hat{P}_{\mu,\nu}\hat{P}_{\mu',\nu'} = \delta_{\nu\mu'}\hat{P}_{\mu,\nu'} \quad (15.6)$$

which can easily be shown by introducing the definition of projection operators in terms of a basis $|\mu\rangle$. The Hamiltonian and the interaction written in terms of these operators are

$$\hat{H}_{\text{loc}} = \sum_{\mu=1}^N h_{\mu,\mu} \hat{P}_{\mu,\mu}, \quad (15.7)$$

$$\hat{V} = \sum_{\mu=1}^{N-1} (v_{\mu,\mu+1} \hat{P}_{\mu,\mu+1} + v_{\mu+1,\mu} \hat{P}_{\mu+1,\mu}), \quad (15.8)$$

with local diagonal Hamiltonian matrices $h_{\mu,\mu}$ and the respective interactions $v_{\mu,\mu+1} = v_{\mu+1,\mu}^\dagger$ due to the Hermiticity of the Hamiltonian (see Fig. 15.2).

In the following we will be interested in the total amount of energy (15.4) in one subunit μ given by the probability of being in the upper band of the respective system

$$P_\mu = \langle \psi_\mu | \psi_\mu \rangle = \langle \psi | \hat{P}_{\mu,\mu} \hat{P}_{\mu,\mu} | \psi \rangle. \quad (15.9)$$

15.2. Dyson Time-Evolution Expansion

Similar to Sect. 6.1.3 we transform the Hamiltonian into the interaction picture and use a Dyson expansion of the time evolution, finding

$$|\psi(\tau)\rangle \approx (\hat{1} - \frac{i}{\hbar} \hat{U}_1 - \frac{1}{\hbar^2} \hat{U}_2) |\psi(0)\rangle, \quad (15.10)$$

with the two time evolution operators (cf. (6.26) and (6.27))

$$\hat{U}_1(\tau) = \int_0^\tau d\tau' \hat{V}(\tau'), \quad \hat{U}_2(\tau) = \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \hat{V}(\tau') \hat{V}(\tau'') \quad (15.11)$$

and the interaction Hamiltonian $\hat{V}(t)$ in the interaction picture. Note that this transformation does not change the block diagonal form of the interaction matrix.

Due to the additive representation of the interaction matrix (15.8) and the definition of the first order time evolution operator (15.11) one may find the same off-diagonal block form for the first order time-evolution operator, too

$$\hat{U}_1 = \sum_{\mu=1}^{N-1} (u_{\mu,\mu+1}^{(1)} \hat{P}_{\mu,\mu+1} + u_{\mu+1,\mu}^{(1)} \hat{P}_{\mu+1,\mu}) . \quad (15.12)$$

The coefficients $u^{(1)}$ contain the respective time dependence and the integration over τ' of the interaction.

For the second order time evolution operator this seems to be more difficult. Besides the sum of single subspace time evolution operators of second order some extra terms survive. Introducing the interaction expanded into projectors (15.8) into the definition of the second order time evolution operator (15.11) one finds

$$\begin{aligned} \hat{U}_2 = & \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \sum_{\mu,\nu} (v_{\mu,\mu+1}(\tau') \hat{P}_{\mu,\mu+1} + v_{\mu+1,\mu}(\tau') \hat{P}_{\mu+1,\mu}) \times \\ & \times (v_{\nu,\nu+1}(\tau'') \hat{P}_{\nu,\nu+1} + v_{\nu+1,\nu}(\tau'') \hat{P}_{\nu+1,\nu}) \end{aligned} \quad (15.13)$$

and with (15.6)

$$\begin{aligned} \hat{U}_2 = & \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \sum_{\mu} \left[v_{\mu,\mu+1}(\tau') v_{\mu+1,\mu}(\tau'') \hat{P}_{\mu,\mu} \right. \\ & + v_{\mu+1,\mu}(\tau') v_{\mu,\mu+1}(\tau'') \hat{P}_{\mu+1,\mu+1} + v_{\mu,\mu+1}(\tau') v_{\mu+1,\mu+2}(\tau'') \hat{P}_{\mu,\mu+2} \\ & \left. + v_{\mu+1,\mu}(\tau') v_{\mu,\mu-1}(\tau'') \hat{P}_{\mu+1,\mu-1} \right] . \end{aligned} \quad (15.14)$$

This operator decomposes into a diagonal and an off-diagonal part

$$\begin{aligned} \hat{U}_2 = & \hat{U}_{\text{diag}} + \hat{U}_{\text{off}} \\ = & \sum_{\mu} (u_{\mu,\mu}^{(2)} \hat{P}_{\mu,\mu} + u_{\mu-1,\mu+1}^{(2)} \hat{P}_{\mu-1,\mu+1} + u_{\mu+1,\mu-1}^{(2)} \hat{P}_{\mu+1,\mu-1}) \end{aligned} \quad (15.15)$$

and a suitable definition of the coefficients $u^{(2)}$.

In the following we will proceed differently from what has been done in the investigation of the decay in Part I. In Chap. 6 we computed the complicated time evolution of a quantity like (15.9) by using the special properties of the projectors and the Hilbert space average itself. In principle it is possible to use this method again, but the technique presented here is more general, in the sense that it is applicable even if the operators $\hat{P}_{\mu,\mu}$ do not constitute a group.

15.3. HAM for Transport Scenario

The time dependence of the probability of finding the excitation in the system μ after a time interval τ in second order is, according to (15.9), given by

$$\begin{aligned} P_\mu(\tau) = \langle \psi(0) | & (\hat{1}\hat{P}_{\mu,\mu}\hat{P}_{\mu,\mu}\hat{1} + \frac{i}{\hbar}\hat{U}_1\hat{P}_{\mu,\mu}\hat{P}_{\mu,\mu}\hat{1} - \frac{i}{\hbar}\hat{1}\hat{P}_{\mu,\mu}\hat{P}_{\mu,\mu}\hat{U}_1 \\ & - \frac{1}{\hbar^2}\hat{1}\hat{P}_{\mu,\mu}\hat{P}_{\mu,\mu}\hat{U}_2 + \frac{1}{\hbar^2}\hat{U}_1\hat{P}_{\mu,\mu}\hat{P}_{\mu,\mu}\hat{U}_1 - \frac{1}{\hbar^2}\hat{U}_2^\dagger\hat{P}_{\mu,\mu}\hat{P}_{\mu,\mu}\hat{1})|\psi(0)\rangle, \end{aligned} \quad (15.16)$$

where we introduced the respective Dyson expansion (15.10) into the probability (15.9). The aim of our further investigations is to rewrite this expression in terms of subspace initial states $|\psi_\mu(0)\rangle$ (cf. (15.5)). Therefore, one has to exchange time evolution operators and projectors. For simplicity we skip the explicit notation of time dependencies in operators and states. Thus, all states will refer to the initial state, in the following.

Since the zeroth order is already the initial probability in the μ th subsystem, we consider all first order terms now. Using (15.6) we find for the operator product

$$\begin{aligned} \hat{U}_1\hat{P}_{\mu,\mu} &= u_{\mu-1,\mu}\hat{P}_{\mu-1,\mu-1}\hat{P}_{\mu-1,\mu} + u_{\mu+1,\mu}\hat{P}_{\mu+1,\mu+1}\hat{P}_{\mu+1,\mu} \\ &= (\hat{P}_{\mu-1,\mu-1} + \hat{P}_{\mu+1,\mu+1})(u_{\mu-1,\mu}\hat{P}_{\mu-1,\mu} + u_{\mu+1,\mu}\hat{P}_{\mu+1,\mu}) \\ &= (\hat{P}_{\mu-1,\mu-1} + \hat{P}_{\mu+1,\mu+1})\hat{U}_1 \end{aligned} \quad (15.17)$$

where the last two reformulations are true since, e.g. products of the kind $\hat{P}_{\mu-1,\mu-1}\hat{P}_{\mu+1,\mu}$ and most others vanish. This identity may be used in all first order terms as well as in the second order terms containing \hat{U}_1 operators in (15.16).

We continue with all terms proportional to \hat{U}_2 . The first part of the operator \hat{U}_{diag} defined in (15.15) is obviously easy to treat since the projector $\hat{P}_{\mu,\mu}$ commutes with this operator directly

$$\hat{P}_{\mu,\mu}\hat{U}_{\text{diag}} = \hat{U}_{\text{diag}}\hat{P}_{\mu,\mu}. \quad (15.18)$$

The operator \hat{U}_{off} is basically the same operator as \hat{U}_1 , but with transitions to the over next neighbor. We get, similar to (15.17),

$$\hat{P}_{\mu,\mu}\hat{U}_{\text{off}} = \hat{U}_{\text{off}}(\hat{P}_{\mu+2,\mu+2} + \hat{P}_{\mu-2,\mu-2}), \quad (15.19)$$

and analogously for the Hermitian conjugate. Finally, (15.16) yields

$$\begin{aligned}
 P_\mu &= \langle \psi_\mu | \psi_\mu \rangle \\
 &+ \frac{i}{\hbar} \left(\langle \psi_{\mu-1} | \hat{U}_1 | \psi_\mu \rangle + \langle \psi_{\mu+1} | \hat{U}_1 | \psi_\mu \rangle \right) \\
 &- \frac{i}{\hbar} \left(\langle \psi_\mu | \hat{U}_1 | \psi_{\mu-1} \rangle + \langle \psi_\mu | \hat{U}_1 | \psi_{\mu+1} \rangle \right) \\
 &+ \frac{1}{\hbar^2} \left(\langle \psi_{\mu-1} | + \langle \psi_{\mu+1} | \right) \hat{U}_1^2 \left(|\psi_{\mu-1}\rangle + |\psi_{\mu+1}\rangle \right) \\
 &- \frac{1}{\hbar^2} \langle \psi_\mu | \left(\hat{U}_{\text{diag}} + \hat{U}_{\text{diag}}^\dagger \right) | \psi_\mu \rangle \\
 &- \frac{1}{\hbar^2} \langle \psi_\mu | \hat{U}_{\text{off}} \left(|\psi_{\mu-2}\rangle + |\psi_{\mu+2}\rangle \right) \\
 &- \frac{1}{\hbar^2} \left(\langle \psi_{\mu-2} | + \langle \psi_{\mu+2} | \right) \hat{U}_{\text{off}}^\dagger | \psi_\mu \rangle
 \end{aligned} \tag{15.20}$$

where all bra and ket vectors refer to the initial state.

Already the zeroth order of all P_μ together fulfills the complete normalization condition of a probability

$$\sum_\mu P_\mu \stackrel{!}{=} 1, \tag{15.21}$$

due to the definition of the vector $|\psi_\mu\rangle$ (cf. (15.9)). Thus, we have to demand that all other orders vanish individually. Obviously, all first order terms cancel out each other. Remaining second order terms

$$\begin{aligned}
 &\sum_\mu \left[\langle \psi_{\mu-1} | \hat{U}_1^2 | \psi_{\mu-1} \rangle + \langle \psi_{\mu+1} | \hat{U}_1^2 | \psi_{\mu+1} \rangle \right. \\
 &\quad \left. + \langle \psi_{\mu-1} | \hat{U}_1^2 | \psi_{\mu+1} \rangle + \langle \psi_{\mu+1} | \hat{U}_1^2 | \psi_{\mu-1} \rangle \right] \\
 &= \sum_\mu \left[\langle \psi_\mu | \left(\hat{U}_{\text{diag}} + \hat{U}_{\text{diag}}^\dagger \right) | \psi_\mu \rangle \right. \\
 &\quad \left. + \langle \psi_\mu | \hat{U}_{\text{off}} | \psi_{\mu-2} \rangle + \langle \psi_\mu | \hat{U}_{\text{off}} | \psi_{\mu+2} \rangle \right. \\
 &\quad \left. + \langle \psi_{\mu-2} | \hat{U}_{\text{off}}^\dagger | \psi_\mu \rangle + \langle \psi_{\mu+2} | \hat{U}_{\text{off}}^\dagger | \psi_\mu \rangle \right]
 \end{aligned} \tag{15.22}$$

lead to the additional conditions

$$\langle \psi_\mu | \hat{U}_{\text{diag}} + \hat{U}_{\text{diag}}^\dagger | \psi_\mu \rangle = 2 \langle \psi_\mu | \hat{U}_1^2 | \psi_\mu \rangle, \tag{15.23}$$

$$\langle \psi_{\mu-1} | \hat{U}_{\text{off}} + \hat{U}_{\text{off}}^\dagger | \psi_{\mu+1} \rangle = \langle \psi_{\mu-1} | \hat{U}_1^2 | \psi_{\mu+1} \rangle. \tag{15.24}$$

So far (15.20) is an exact equation of motion for the excitation probability of subunit μ . We approximate this equation by replacing the right hand side by its Hilbert space average. The concrete evaluation is rather lengthy and has been summarized in App. C. All Hilbert space averages of quantities with states of completely different subspaces on the left and right hand side of an arbitrary operator vanish (cf. (C.15-C.17)). Furthermore, using the conditions (15.23) we get

$$P_\mu = \langle \psi_\mu | \psi_\mu \rangle - \frac{2}{\hbar^2} [\langle \psi_\mu | \hat{U}_1^2 | \psi_\mu \rangle] \\ + \frac{1}{\hbar^2} [\langle \psi_{\mu+1} | \hat{U}_1^2 | \psi_{\mu+1} \rangle] + \frac{1}{\hbar^2} [\langle \psi_{\mu-1} | \hat{U}_1^2 | \psi_{\mu-1} \rangle]. \quad (15.25)$$

Such Hilbert space averages are well-known and can be found in [40]. Using (C.18) we further simplify the above equation to

$$P_\mu(\tau) = \langle \psi_\mu | \psi_\mu \rangle - \frac{2}{\hbar^2} \frac{\langle \psi_\mu | \psi_\mu \rangle}{n} \text{Tr}_\mu \{ \hat{U}_1^2 \} \\ + \frac{1}{\hbar^2} \frac{\langle \psi_{\mu+1} | \psi_{\mu+1} \rangle}{n} \text{Tr}_{\mu+1} \{ \hat{U}_1^2 \} \\ + \frac{1}{\hbar^2} \frac{\langle \psi_{\mu-1} | \psi_{\mu-1} \rangle}{n} \text{Tr}_{\mu-1} \{ \hat{U}_1^2 \}. \quad (15.26)$$

The calculation of the traces is done as in Sect. 8.1.3 finally getting, in the special case for equally sized subspaces

$$\text{Tr}_\mu \{ \hat{U}_1^2 \} = \left| \int_0^\tau d\tau' \text{Tr} \{ \hat{V}(\tau') \} \right|^2 \approx \frac{2\pi\hbar\lambda^2 n^2 \tau}{\delta\epsilon}. \quad (15.27)$$

Defining the decay constant

$$\kappa := \frac{2\pi\lambda^2 n}{\hbar\delta\epsilon} \quad (15.28)$$

and remembering that $\langle \psi_\mu | \psi_\mu \rangle := P_\mu(0)$ one finds

$$P_\mu(\tau) = P_\mu(0) - \kappa \left(2P_\mu(0) - P_{\mu+1}(0) - P_{\mu-1}(0) \right) \tau. \quad (15.29)$$

The above approximation for the trace of the square of the time-evolution operator (15.27) is only valid in the time interval $\tau_1 < \tau < \tau_2$ (see Sect. 8.2) from which we derive the two conditions for the linear regime

$$\frac{\lambda}{\delta\epsilon} n \geq \frac{1}{2}, \quad \frac{\lambda^2}{\delta\epsilon^2} n \ll 1. \quad (15.30)$$

As long as these conditions are fulfilled the given second order time evolution approximation is valid and one may iterate (15.29)

$$\frac{P_\mu((i+1)\tau) - P_\mu(i\tau)}{\tau} = -\kappa \left(2P_\mu(i\tau) - P_{\mu+1}(i\tau) - P_{\mu-1}(i\tau) \right). \quad (15.31)$$

In the limit of τ being extremely small we find the respective *rate equation* for the system. Since the system is a finite chain of N subsystems we get a slightly different equation for the first and the last system in the chain. The complete system of differential equations reads

$$\frac{dP_1}{dt} = -\kappa(P_1 - P_2), \quad (15.32)$$

$$\frac{dP_\mu}{dt} = -\kappa \left(2P_\mu - P_{\mu+1} - P_{\mu-1} \right), \quad \mu = 2, \dots, N-1, \quad (15.33)$$

$$\frac{dP_N}{dt} = -\kappa(P_N - P_{N-1}). \quad (15.34)$$

This rate equation constitutes a statistical behavior of the model system under the fulfillment of the conditions (15.30). Before we discuss this model with respect to heat conduction, we compare the above rate equation behavior with the exact Schrödinger evolution of the given model system in the next Chapter.

16. Diffusive Behavior from Schrödinger Dynamics

Until recently it was believed that the laws of statistical mechanics were applicable only to systems with many degrees of freedom. [...] we ask whether the deterministic evolution of quantum systems with a few degrees of freedom can also exhibit statistical behavior.

R.V. Jensen and R. Shankar in [71]

In the last Chapter we have introduced a new theoretical tool – the *Hilbert Space Average Method* (HAM) – to investigate the decay into the global equilibrium from a nonequilibrium initial state. For the model class defined by the conditions (cf. (15.30)), we expect a statistical behavior – an exponential relaxation. Despite the underlying time reversible Schrödinger dynamics, this statistical relaxation process simply follows a *rate equation* (15.32)-(15.34).

To show that such a behavior is indeed feasible directly from the Schrödinger equation, we will present some numerical data of the decay in the system depicted in Fig. 15.1 to support the above theoretical prediction. Furthermore, we will investigate the limits of the given theory, such as the dependence on the concrete initial state and the system size.

16.1. Decay Behavior of a Model System

To analyze the validity and performance of HAM we compare its results with data from a direct numerical integration of the Schrödinger equation. This is, of course, only possible for systems that are small enough to allow for the latter. Hereby, we restrict ourselves to initial states with only one subsystem in the excited band (all others in the ground level, black dots in Fig. 15.1). Finding an effective Hamiltonian for the one-excitation subspace we are able to solve the Schrödinger equation for up to $N = 10$ subsystems, $n = 500$ levels each.

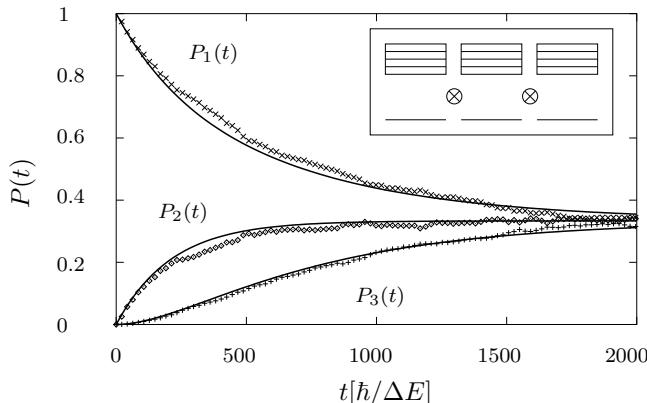


Figure 16.1.: Probability to find the excitation in one of the three subunits (inset); exact Schrödinger dynamics (dots) compared to the solution of the rate equations (16.3)-(16.5). Parameters: $N = 3$, $n = 500$, $\lambda = 5 \cdot 10^{-5}$, $\delta\epsilon = 0.005$.

For the comparison we use a model system consisting of $N = 3$ and $N = 5$ subunits, respectively with $n = 500$ levels each in the band of width $\delta\epsilon = 0.005$. The subunits are coupled by an energy exchanging next neighbor interaction with strength $\lambda = 5 \cdot 10^{-5}$ ($\Delta E = 1$). The interaction is chosen to be a normalized Hermitian matrix. Thus, the total Hamiltonian of the system refers to the matrix structure in Fig. 15.2. For these special system parameters the criteria (15.30) read

$$\frac{\lambda}{\delta\epsilon}n = 5 \geq \frac{1}{2}, \quad \frac{\lambda^2}{\delta\epsilon^2}n = 0.05 \ll 1. \quad (16.1)$$

Since these criteria are fulfilled, HAM should be applicable and we expect the system to behave statistically. The decay time, the inverse of the rate κ , is according to the theoretical considerations of the last Chapter (cf. (15.28)) given by

$$\tau = \frac{1}{\kappa} = \frac{\hbar\delta\epsilon}{2\pi\lambda^2n} = 636.6 [\hbar/\Delta E]. \quad (16.2)$$

We first examine the system with $N = 3$, and with an initial state where the excitation is localized in the first system, all others are initially in their ground state ($P_1(0) = 1$, $P_2(0) = P_3(0) = 0$). The solution of the appropriate

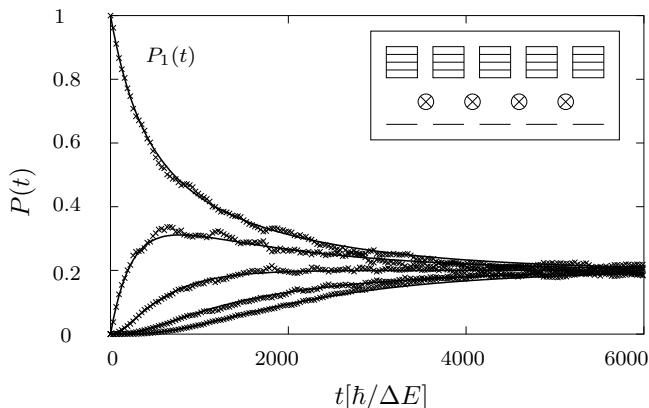


Figure 16.2.: Probability to find the excitation in one of the five subunits (inset); exact Schrödinger dynamics (dots) compared to the solution of the rate equations (15.32)-(15.34). Parameters: $N = 5$, $n = 500$, $\lambda = 5 \cdot 10^{-5}$, $\delta\epsilon = 0.005$.

rate equation reads

$$P_1(t) = \frac{1}{6}(2 + e^{-3t/\tau} + 3e^{-t/\tau}), \quad (16.3)$$

$$P_2(t) = \frac{1}{3}(1 - e^{-3t/\tau}), \quad (16.4)$$

$$P_3(t) = \frac{1}{6}(2 + e^{-3t/\tau} - 3e^{-t/\tau}). \quad (16.5)$$

In Fig. 16.1 we show the full solution of the Schrödinger equation together with the HAM prediction. Lines refer to (16.3)-(16.5) whereas dots are the results of the integration of the Schrödinger equation. In Fig. 16.2 the same is done for $N = 5$ subunits based on an appropriate solution of (15.32)-(15.34). Besides some fluctuations (finite size effects) the HAM prediction shows a very good agreement with the exact solution.

16.2. Fluctuations and Size Effects

To investigate the accuracy of the HAM we introduce a measure for the deviation of the exact Schrödinger result from the HAM prediction. In order to investigate this deviation in dependence of the subsystem size n we use the time-averaged quadratic deviation D_1^2 of the exact solution from the rate

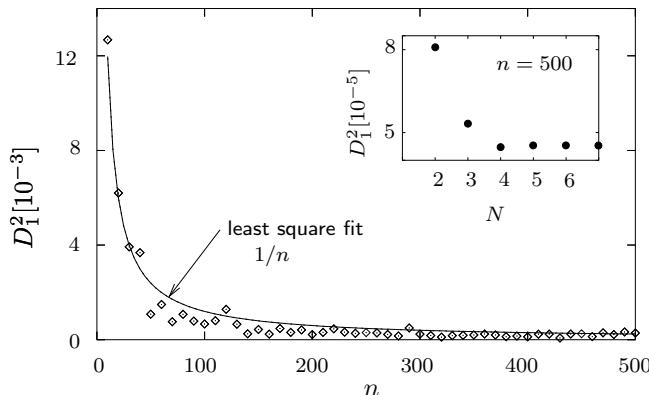


Figure 16.3.: Deviation of HAM from the exact solution (D_1^2 least squares): dependence of D_1^2 on n for $N = 3$. Inset: dependence of D_1^2 on N for $n = 500$.

equations (15.32-15.34) concentrating on the probability of being in the excited band of the first system $P_1(t)$ for the moment. Here the deviation is defined by the least square

$$D_1^2 = \frac{1}{5\tau} \int_0^{5\tau} \left[P_1^{\text{HAM}}(t) - P_1^{\text{exact}}(t) \right]^2 dt , \quad (16.6)$$

integrating up to a multiple of the decay time τ (cf. (16.2)). We thus estimate the fluctuations on the way to equilibrium, no equilibrium fluctuations are considered.

To analyze how big the “typical deviation” is we have computed D_1^2 for the $N = 3$ system with the first subunit initially in an arbitrary excited state and for different numbers of states n in the upper bands of the subunits. As shown in Fig. 16.3, the deviation scales like $1/n$ with the band size, i.e. vanishes in the limit of high dimensional subunits. This behavior does not come as a surprise since it has already theoretically been conjectured and numerically verified in the context of equilibrium fluctuations of non-Markovian systems [10, 40].

The inset of Fig. 16.3 shows that D_1^2 also decreases with an increasing number of subunits N , but then levels off. Therefore it seems that some fluctuations remain even for infinite systems, i.e. in the limit of $N \rightarrow \infty$. However, note that this result refers to “nonequilibrium” fluctuations on the way to equilibrium. On the other hand, equilibrium fluctuations scale with one over the total amount of states and thus vanish in the thermodynamic

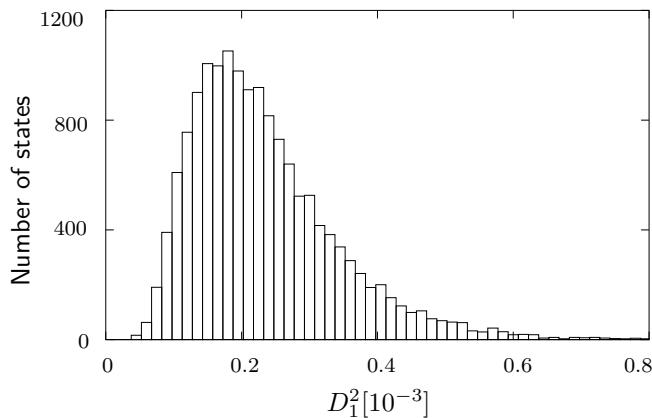


Figure 16.4.: Deviation of HAM from the exact solution ($D_1^2 \leq 1$ least squares) for 15000 equally distributed initial states ($N = 2$, $n = 500$).

limit, i.e. for infinite systems¹. At least asymptotically, when the system has “experienced” its full dimensions, it will fluctuate only, if it is finite. Thus, all fluctuations observed so far are only finite size effects of the systems under consideration.

In conclusion HAM appears to be applicable even down to moderately sized systems. So far we have restricted ourselves to pure states. A drastic further reduction of D^2 can be expected for mixed states (which are typical in the context of thermodynamical phenomena), since pure state fluctuations may be expected to cancel partially if added together.

16.3. Initial States

To check the validity of HAM with respect to different pure initial states we have computed D^2 for 15000 equally distributed initial states, for a $N = 2$ subunit system with one subunit in the upper band and the other subunit in its ground state. Both subunits have $n = 500$ levels in their band and are coupled as before with strength $\lambda = 5 \cdot 10^{-5}$.

As initial states we choose some equally distributed states of the subregion of Hilbert space where the first system is in its upper band, the second one

¹In a private conversation with G. Mahler the author earned the opinion that fluctuations are always a result of the finite size of the considered system. In any infinite system and at the end of the whole decay no fluctuations remain.

in its ground state. In order to produce such equally distributed states in the respective subspace we use Gaussian distributed real and imaginary numbers (with zero mean and variance one) for the complex amplitudes of the states. (For a detailed investigation on equally distributed states in a Hilbert space compartment see [112].)

The results of the investigation are condensed into the histogram shown in Fig. 16.4. Note that the deviation is really small (maximum possible value of D_1^2 is one), even for the states at the right hand side of the picture.

Obviously, almost all initial states lead to approximately the same small deviation. Thus, a good agreement of HAM with the exact result may safely be expected regardless of HAM being a best guess only; accidentally one may get a poor agreement. But, in fact this is the essence of most thermodynamic statements: They hold typically, but not always.

17. Transport Coefficients

One of the most fundamental notions in the theory of interacting many-particle systems is that (almost) nothing that is physically interesting, can be calculated rigorously from first principles. Once this has been recognized – sometime within the first year of graduate study – it becomes of crucial importance for those not inclined to give up to hide their potential ignorance of complicated details away in places where it is least likely to cause harm.

D. Forster in [32]

In the last Chapter we have shown that a statistical decay from a nonequilibrium initial state into the global equilibrium final state is indeed feasible, just based on Schrödinger dynamics of the complete system. The prediction of the Hilbert space average method (HAM) has been found to be in very good accordance with the exact solution, which is also supported by an investigation of deviations from the HAM solution.

In the present Chapter we analyze systems for which the criteria for the applicability of HAM are fulfilled. Thus, we directly use the results of Chap. 15 for the decay in such systems proper addressing the heat respectively energy current. By a comparison of this current with Fourier's Law we are then able to extract the respective transport coefficient the *energy diffusion constant* or the *heat conductivity*.

17.1. Energy Transport

Considering the model system introduced in Fig. 15.1, but, for simplicity with $N = 2$ subunits, we can adjust the parameters such that the criteria for a diffusive behavior are fulfilled. Thus, the system behaves due to the rate equation derived in Sect. 15.3 resulting finally into (15.32). Furthermore, one

finds for the decay constant (15.28) from theoretical considerations

$$\kappa = \frac{2\pi\lambda^2 n}{\hbar\delta\epsilon} . \quad (17.1)$$

In order to account for the energy diffusion constant in the given model system, we have to consider the energy current inside the system. This current is defined by the change of the internal energy U_μ of the two corresponding subunits

$$J = \frac{1}{2} \left(\frac{dU_1}{dt} - \frac{dU_2}{dt} \right) . \quad (17.2)$$

The total internal energy in a subunit of the above described type is given by the probability to be in the excited band of the subunit times the width of the energy gap, $U_\mu = \Delta E P_\mu$. Thus, we may reformulate the current due to the change of the probability being in the excited band, finding

$$J = \frac{\Delta E}{2} \left(\frac{dP_1}{dt} - \frac{dP_2}{dt} \right) . \quad (17.3)$$

The change of the probability in time is given by the rate equation (15.32) derived under some preconditions for the model parameters, we assume to be fulfilled here. Plugging in the respective rate equation one finds for the current

$$J = -\kappa \Delta E (P_2 - P_1) . \quad (17.4)$$

In the general situation of more subunits the consideration is quite similar. However, note that the current definition is more complicated since the energy change in subunit μ leads to a current to both sides

$$\frac{dU_\mu}{dt} = \Delta E \frac{dP_\mu}{dt} = J(\mu - 1, \mu) - J(\mu, \mu + 1) , \quad (17.5)$$

where the sign is defined by the direction of the current (cf. Chap. 11). This equation is a discrete version of the continuity equation for the energy in subsystem μ . By a comparison with the rate equation (15.33) the system is subject to, one may identify the current from subsystem μ to $\mu + 1$ with

$$J(\mu, \mu + 1) = -\kappa \Delta E (P_{\mu+1} - P_\mu) = -\kappa (U_{\mu+1} - U_\mu) . \quad (17.6)$$

We find the current to be a linear function of the probability gradient respectively *energy gradient* inside the system. This is a diffusive behavior since

energy diffuse through the system in a statistical way. Therefore we may extract the energy diffusion constant from the above equation, identifying the parameter κ from the rate equation with the transport coefficient given in (17.1). This energy diffusion constant depends on the coupling strength of the subunits λ and on the state density of the excited band $n/\delta\epsilon$.

Remarkably this diffusive behavior does not need an initially small energy gradient. Think, e.g., of the initial state of the last Chapter with all energy in the first system nothing in all others. This is a state far away from the final expected equilibrium – equipartition of energy in the system. But, nevertheless, one can find a statistical diffusive behavior.

17.2. Heat Transport

So far we have only considered the energy transport through the system on the route from a nonequilibrium initial state to a global equilibrium final state. Of course this could be transferred in some sense to heat transport since heat is nothing else but thermal energy. Nevertheless, we may face some difficulties by investigating the heat transport, for the reason of being far away from equilibrium in all former investigation.

Usually we have started with an initial state, where the first system is completely in its exited band, all others are in their ground states (cf. the system depicted in Fig. 15.1 and the decay behavior in Fig. 16.1). By a simple transfer to temperatures by fitting a Boltzmann distribution this state would feature a strange temperature profile: the first system is at negative, all others at zero temperature. Nobody would expect a normal heat conduction behavior in such a far from equilibrium situation. Nevertheless, the energy transport is statistical although being initially far from equilibrium (see Chap. 15 and the last Section). Thus, we should consider another initial state already near the final global equilibrium state, featuring only a small gradient. In this investigations we will also use a pure state observing its decay by solving the Schrödinger equation as before. Finally, summing over many pure state trajectories one gets the time evolution of an initially mixed state. But, if it is indeed possible to find heat diffusion for pure states we are sure that one may find it also for mixed ones, even with reduced fluctuations.

17.2.1. Thermal Initial State

We restrict ourselves in the following to only two subunits, but taking immediately a more complicated structure with more than one exited band per subunit into account. The model system is shown in Fig. 17.1, especially for

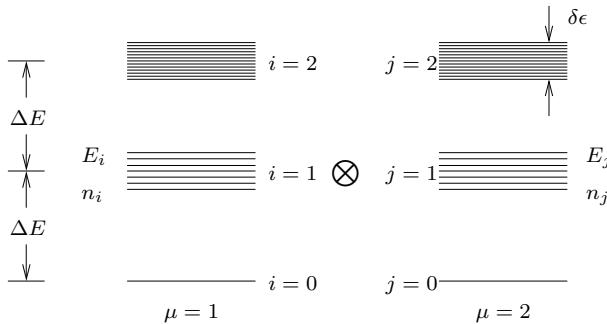


Figure 17.1.: Heat conduction model with more excited bands: each band consists of n_i equally distributed levels.

three bands. In general the considerations in the following are also valid for an arbitrary number of bands in each subunit. The index i is reserved for the left, j for the right system. We take a product state

$$|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle \quad (17.7)$$

as the initial state for all further investigations. We expect similar results for the present investigation as in Chap. 15.

For the single subsystem states we choose a *quasi thermal state* with temperature β_μ , i.e. a *superposition* of states according to the Boltzmann distribution. “Quasi” means here that this state is *not* a mixed state as usual for thermal states, but a pure one. Furthermore, we treat the bands as degenerate since the band width is much smaller than the gap $\delta\epsilon \ll \Delta E$. Thus, the levels inside the band are equally occupied according to the temperature β_μ . The probability distribution of the first subsystem depending on the band energy E_i and the appropriate number of states n_i in the band is therefore given by

$$P_1(E_i) = \frac{n_i e^{-\beta_1 E_i}}{Z(\beta_1)} , \quad (17.8)$$

with the partition function $Z(\beta_1)$. The second subsystem distribution is obtained simply by exchanging i by j and the respective quantities of the second subsystem.

The quantity of interest is the probability distribution of the whole system. Since the total state is a product state the probability distribution of the complete system state P_{ij} is simply the product of the single probabilities. We can formulate this distribution function in terms of the two single system

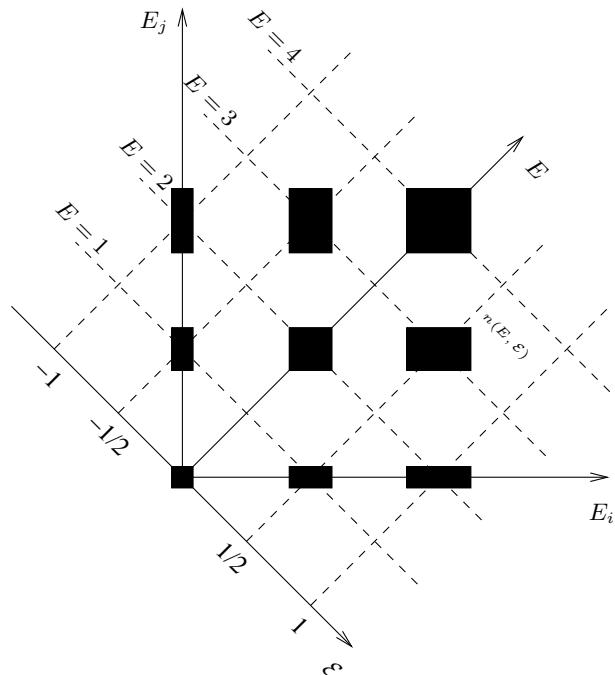


Figure 17.2.: Alternative scheme to depict the complete multi-band spectrum: individual spectra of the two subunits on the E_i , E_j axes respectively; transformation to the new parameters (E, \mathcal{E}) ; black bands indicate the complete spectrum. Examples: $(E, \mathcal{E}) = (1, -1/2)$ are states, where the first system is in its first band, the second one in its ground state, $(E, \mathcal{E}) = (2, 0)$ are states, where both systems are in the first excited band etc.

energies E_i and E_j

$$P_{ij} = \frac{n_i e^{-\beta_1 E_i}}{Z(\beta_1)} \frac{n_j e^{-\beta_2 E_j}}{Z(\beta_2)}. \quad (17.9)$$

However, it is convenient here to use a new set of coordinates for the combined spectrum in terms of the mean energy E of a band in the whole system and some energy displacement \mathcal{E}

$$E := E_i + E_j, \quad \mathcal{E} := \frac{1}{2}(E_i - E_j). \quad (17.10)$$

All energies, including E and \mathcal{E} , are measured in units of ΔE . To support intuition we show both sets of coordinates in Fig. 17.2: The full spectrum

(black bands) can either be characterized in terms of the single subsystem spectra (E_i, E_j) or by (E, \mathcal{E}) . The latter coordinates appear as a 45° -rotation of the original ones.

We define the number of levels per band (E, \mathcal{E}) as $n(E, \mathcal{E}) = n_i n_j$ (see Fig. 17.2). Using (17.10) to transform the probability distribution (17.9) to the new parameter set, the total system probability reads

$$P(E, \mathcal{E}) = \frac{n(E, \mathcal{E})}{Z(\beta_1)Z(\beta_2)} \exp\left(-\beta_1 \frac{E + 2\mathcal{E}}{2} - \beta_2 \frac{E - 2\mathcal{E}}{2}\right). \quad (17.11)$$

Introducing now a small temperature gradient ΔT around a mean temperature T according to

$$\beta_1 = \frac{1}{k_B(T + \frac{\Delta T}{2})}, \quad \beta_2 = \frac{1}{k_B(T - \frac{\Delta T}{2})} \quad (17.12)$$

one finds the probability distribution

$$\begin{aligned} P(E, \mathcal{E}) &= \frac{n(E, \mathcal{E})}{Z(\beta_1)Z(\beta_2)} \exp\left(-\frac{E + 2\mathcal{E}}{2k_B(T + \frac{\Delta T}{2})} - \frac{E - 2\mathcal{E}}{2k_B(T - \frac{\Delta T}{2})}\right) \\ &= \frac{n(E, \mathcal{E})}{Z(\beta_1)Z(\beta_2)} \exp\left(-\frac{ET - \mathcal{E}\Delta T}{k_B(T^2 - (\frac{\Delta T}{2})^2)}\right). \end{aligned} \quad (17.13)$$

In order to get a near equilibrium situation the temperature gradient ΔT has to be very small in comparison to the mean temperature $\Delta T \ll T$. Therefore we expand the exponential function in (17.13) in terms of ΔT finding in first order

$$P(E, \mathcal{E}) = \frac{n(E, \mathcal{E})e^{-\frac{E}{k_B T}}}{Z(\beta_1)Z(\beta_2)} \left(1 + \frac{\mathcal{E}}{k_B T^2} \Delta T + \mathcal{O}(\Delta T^2)\right). \quad (17.14)$$

The product of partition functions in the denominator of the probability distribution is defined as

$$Z(\beta_1)Z(\beta_2) = \sum_i n_i e^{-\beta_1 E_i} \sum_j n_j e^{-\beta_2 E_j}. \quad (17.15)$$

Since the difference in the temperatures is very small we can expand each of the exponentials in terms of ΔT . Using only the lowest order we may approximate the above product of partition functions as

$$Z(\beta_1)Z(\beta_2) \approx \sum_{ij} n_i n_j e^{-\frac{E_i + E_j}{k_B T}}. \quad (17.16)$$

Switching to the new parameters we get

$$Z(\beta_1)Z(\beta_2) \approx \sum_{E,\mathcal{E}} n(E, \mathcal{E}) e^{-\frac{E}{k_B T}} =: Z(T). \quad (17.17)$$

Therefore the complete system state is a thermal equilibrium state of the whole system with temperature T and a small linear deviation according to the temperature gradient ΔT

$$P(E, \mathcal{E}) \approx \frac{n(E, \mathcal{E}) e^{-\frac{E}{k_B T}}}{Z(T)} \left(1 + \frac{\mathcal{E}}{k_B T^2} \Delta T \right). \quad (17.18)$$

17.2.2. Current

In the following we consider the energy current between the two subsystems. This quantity is defined as the change of the energy in the first minus the change of the energy in the second system – as before a sort of continuity equation for the local energy. The total energy U_μ in, e.g. the first subunit, is given by

$$U_1 = \sum_i E_i P_i, \quad (17.19)$$

where P_i is the time dependent energy distribution in the first system. To get the respective first system probability distribution P_i from the time dependent full system probability distribution P_{ij} we have to trace over the second subsystem finding

$$U_1 = \sum_{ij} E_i P_{ij} \quad (17.20)$$

According to this total energy in one subsystem the current reads

$$\begin{aligned} J &= \frac{1}{2} \left(\frac{dU_1}{dt} - \frac{dU_2}{dt} \right) \\ &= \frac{1}{2} \sum_{ij} \left(E_i \frac{dP_{ij}}{dt} - E_j \frac{dP_{ij}}{dt} \right), \end{aligned} \quad (17.21)$$

or, switching to the new parameters (cf. (17.10))

$$J = \sum_{E,\mathcal{E}} \mathcal{E} \frac{d}{dt} P(E, \mathcal{E}). \quad (17.22)$$

For a single band model the sum over E would break down and we recover the result (17.3).

The change of the probability $P(E, \mathcal{E})$ is again described by the rate equation according to the HAM. Since the complete model decomposes into several energy subspaces, the derivation is essentially just as given in Chap. 15. The respective energy transport coefficient results as a more complicated form depending on the band it belongs to ($\kappa = \kappa(E, \mathcal{E}, \mathcal{E}')$). However, we require that κ is symmetric under the exchange of \mathcal{E} and \mathcal{E}' , since the energy transport from system $\mu = 1$ to system $\mu = 2$ should be as good as in the reverse direction. Therefore we end up with the rate equation

$$\frac{d}{dt}P(E, \mathcal{E}) = -\sum_{\mathcal{E}'}\kappa(E, \mathcal{E}, \mathcal{E}')\left(P(E, \mathcal{E}) - P(E, \mathcal{E}')\right). \quad (17.23)$$

The fact that κ depends on the respective band is already obvious from (17.1) which depends on the state density of the band. Plugging in the rate equation (17.23), derived according to the Hilbert space average method of Chap. 15, into the current (17.22) we find

$$J = -\sum_{E, \mathcal{E}, \mathcal{E}'}\mathcal{E}\kappa(E, \mathcal{E}, \mathcal{E}')\left(P(E, \mathcal{E}) - P(E, \mathcal{E}')\right). \quad (17.24)$$

Thus, it turns out that the current is simply a function of the actual state.

17.2.3. Heat Conductivity

For a short time step, we may use the first order approximation of the “quasi” thermal initial state (17.18). Since we are summing over \mathcal{E} and \mathcal{E}' the zeroth order terms, according to (17.18) will cancel. The remaining first order part

$$J = -\sum_{E, \mathcal{E}, \mathcal{E}'}\frac{\kappa(E, \mathcal{E}, \mathcal{E}')}{k_B T^2}\frac{e^{-\frac{E}{k_B T}}}{Z(T)}\left(n(E, \mathcal{E})\mathcal{E}^2 - n(E, \mathcal{E}')\mathcal{E}\mathcal{E}'\right)\Delta T, \quad (17.25)$$

gives a heat current proportional to the temperature difference ΔT . By comparing this current with Fourier’s Law $J = -\kappa_{\text{th}}\Delta T$ (10.7) one can extract the heat transport coefficient as

$$\kappa_{\text{th}} = \sum_{E, \mathcal{E}, \mathcal{E}'}\frac{\kappa(E, \mathcal{E}, \mathcal{E}')}{k_B T^2}\frac{e^{-\frac{E}{k_B T}}}{Z(T)}\left(n(E, \mathcal{E})\mathcal{E}^2 - n(E, \mathcal{E}')\mathcal{E}\mathcal{E}'\right) \quad (17.26)$$

a quantity depending only on parameters of the respective model system and on temperature. This is a very general formula for the heat conductivity

derived from HAM, valid for the class of model systems depicted in Fig. 17.1 with an arbitrary number of bands.

Returning to the single band model as shown in Fig. 15.1, we formulate the probability distribution and the current in terms of the new parameters. With $E = \Delta E$, $\mathcal{E} = \pm \Delta E/2$ (cf. Fig. 17.2) the HAM rate equation yields

$$\frac{d}{dt} P(\Delta E, \Delta E/2) = -\kappa \left(P(\Delta E, \Delta E/2) - P(\Delta E, -\Delta E/2) \right), \quad (17.27)$$

cf. (15.32). Here, the energy diffusion constant (17.1) is unique, i.e. does not depend on the system energy.

The sum over the mean band energy E in the current (17.22) vanishes, so that

$$\begin{aligned} J &= \sum_{\mathcal{E}} \mathcal{E} \frac{d}{dt} P(\Delta E, \mathcal{E}) \\ &= \frac{\Delta E}{2} \left(\frac{d}{dt} P(\Delta E, \Delta E/2) - \frac{d}{dt} P(\Delta E, -\Delta E/2) \right). \end{aligned} \quad (17.28)$$

The time derivative of the probability is given by the rate equation (17.27). Thus, we get for the current

$$J = -\kappa \Delta E \left(P(\Delta E, \Delta E/2) - P(\Delta E, -\Delta E/2) \right). \quad (17.29)$$

Furthermore, plugging the respective “quasi” thermal probability distribution (17.18) into this equation yields

$$J = -\frac{\kappa}{2k_B} \frac{e^{-\frac{\Delta E}{k_B T}}}{Z(T)} \frac{\Delta E^2 \Delta T}{T^2} \left(n(\Delta E, \Delta E/2) + n(\Delta E, -\Delta E/2) \right). \quad (17.30)$$

Using the energy diffusion coefficient κ defined in (17.1) and realizing that $n(\Delta E, \Delta E/2) = n(\Delta E, -\Delta E/2) = n$ we can further simplify (17.30) getting

$$J = -\frac{2\pi\lambda^2 n^2}{\hbar k_B \delta\epsilon} \frac{e^{-\frac{\Delta E}{k_B T}}}{Z(T)} \frac{\Delta E^2}{T^2} \Delta T. \quad (17.31)$$

By a comparison with Fourier’s Law, we find the heat conductivity of the single band model

$$\kappa_{\text{th}} = \frac{2\pi k_B \lambda^2 n^2}{\hbar \delta\epsilon} \frac{e^{-\frac{\Delta E}{k_B T}}}{Z(T)} \left(\frac{\Delta E}{k_B T} \right)^2. \quad (17.32)$$

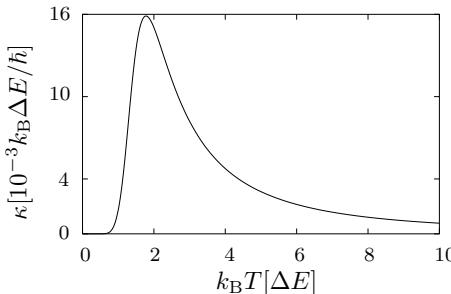


Figure 17.3.: Heat conductivity (17.35) over temperature for a system depicted in Fig. 15.1 ($n = 500$, $\delta\epsilon = 0.05$, $\lambda = 5 \cdot 10^{-5}$).

The partition function of a single subunit reads

$$Z(\beta_1) = 1 + ne^{-\beta_1 \Delta E}. \quad (17.33)$$

Using the same approximation of the partition function product as in (17.16) we find

$$Z(\beta_1)Z(\beta_2) \approx \left(1 + ne^{-\frac{\Delta E}{k_B T}}\right)^2 = Z(T). \quad (17.34)$$

Finally, this gives rise to the heat conductivity of the special model depicted in 15.1

$$\kappa_{\text{th}} = \frac{2\pi k_B \lambda^2 n}{\hbar \delta\epsilon} \frac{ne^{-\frac{\Delta E}{k_B T}}}{\left(1 + ne^{-\frac{\Delta E}{k_B T}}\right)^2} \left(\frac{\Delta E}{k_B T}\right)^2. \quad (17.35)$$

The dependency of the transport coefficient κ_{th} on temperature is displayed in Fig. 17.3. It roughly looks as expected for typical isolating solids. There is no $\propto T^3$ behavior for small temperatures which is, however, only to be expected for three dimensional crystal lattices with a linear phonon dispersion relation for small momenta. The exponential behavior for small temperatures $\propto \exp(-1/T)$ results from the gap in the system and is difficult to treat since it is an essential singularity. This is a well-known result for systems featuring a large energy gap. Furthermore, we find a $\propto T^{-2}$ behavior rather than the usual $\propto T^{-1}$ behavior in the high temperature limit. Again, the usual $\propto T^{-1}$ is no rigorous general result, Peierls only states that the exponent should be between minus one and minus two as discussed in Sect. 10.3.

17.3. Connection between Heat and Energy Transport

We finally consider the connection of the heat conductivity (17.35) with the energy conductivity (17.1). The canonical partition function of a single sub-unit reads

$$Z = 1 + ne^{-\beta \Delta E}. \quad (17.36)$$

The heat capacity (see e.g. [135]) in terms of the partition function is defined as

$$c = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (17.37)$$

Thus, it follows for the heat capacity of a single subunit

$$c = k_B \cdot \frac{ne^{-\frac{\Delta E}{k_B T}}}{\left(1 + ne^{-\frac{\Delta E}{k_B T}}\right)^2} \left(\frac{\Delta E}{k_B T}\right)^2. \quad (17.38)$$

From a comparison with the heat conductivity (17.35) of the last Section one derives a relation between the heat transport and the energy transport coefficient

$$\kappa_{\text{th}} = \frac{2\pi\lambda^2 n}{\hbar\delta\epsilon} c = \kappa c. \quad (17.39)$$

Therefore we find the heat conductivity to be proportional to the heat capacity of the subunits c and the energy diffusion constant κ .

18. Conclusion and Outlook

The time will come, when mental acumen and prolonged study will bring to light what is now hidden ... the time will come when our successors will wonder how we could have been ignorant of things so obvious.

Lucius Annaeus Seneca [139]

We have shown that the consideration of both relaxation as well as transport processes on the basis of the same theoretical tool – the *Hilbert Space Average Method* – is indeed feasible. According to those investigations both phenomena directly follow from first principles, here quantum mechanics. Finally, those considerations could allow for a combined theoretical understanding of the apparently separated fields of relaxation and transport processes within a single quantum thermodynamic approach.

Previously we had realized that a system coupled to a surprisingly small quantum mechanical environment finally reaches an equilibrium state featuring the standard properties of the thermal equilibrium: a maximum value of entropy and in case of an energy exchanging contact with its environment (canonical situation) a well defined temperature, too. Within the present work we have been able to show that this final equilibrium is furthermore reached via diffusive transport or a statistical decay. Nevertheless, the system is microscopically governed by reversible quantum dynamics, irreversible behavior emerges on a mesoscopic level.

Using the Hilbert Space Average Method we have found a statistical decay in a class of small quantum systems coupled to a finite environment. Furthermore, theory provides us with some criteria to judge whether a given system belongs to the class of statistically behaving systems or not. In general, theory gives a closed rate equation for the system, on the basis of occupation probabilities of energy subspaces. In some special cases we even get a rate equation for the density operator of the system. The dynamical properties of the system are thus influenced by some parameters, like temperature and coupling strength of the reservoir, only. However, there is no concrete dynamical variable of the environment included. This opens the way to discuss thermalization and decoherence processes in nanoscopic quantum systems like

e.g. a two level atom coupled to a single molecule or a quantum dot as an environment proper.

Furthermore, it was possible to point out the difficulties of some standard approaches, by using them in finite environment models. However, especially in transport models, coarse grained parts of the whole system are embedded in their finite surrounding, and thus the new method dealing with finite systems is crucial, in order to correctly describe the situation. Thus, we have used the Hilbert Space Average Method to investigate the transport process of energy respectively heat through chains of mesoscopic quantum subunits, too. Under certain constraints as e.g. a weak coupling between adjacent subunits, we were able to identify statistical behavior in such chains. Besides the topological structure of the system in real space the type of observation is important, here. For a proper emergence of diffusive behavior we have to consider the system in a coarse grained way, i.e. asking for properties of the entire subunit, not for the concrete microscopic state. Investigating a quantum system proper as above diffusive transport of energy and heat through the system is indeed feasible. Finally, it was possible to completely reduce *Fourier's Law* and thus diffusive transport to fundamental principles, here to Schrödingerian quantum dynamics.

Besides the quantum thermodynamic scheme we have also considered transport within a quantum master equation approach, by extending the standard Kubo formula from Hilbert to Liouville space. In this way, we were able to investigate transport properties of explicit microscopic model systems, such as spin chains. According to these methods it was possible to concretely account for material parameters like the heat conductivity, discussing the type of transport in dependence of the model class as well as external and internal parameters.

Both, the Hilbert Space Average Method and the perturbation theory in Liouville space, have opened new perspectives towards the investigation of statistical behavior in small quantum system near the global equilibrium. Several interesting open questions remain which hopefully will be answered in the near future. Those questions mainly address the relationship between the presented new methods, the Hilbert Space Average Method and the Kubo formula in Liouville space as well as the connection to some other important theoretical concepts like the standard Kubo formula, the quasiparticle approach, quantum chaos etc. Work is in progress to apply the new methods to other concrete models and to discuss differences between the theoretical predictions. However, until now the application of the Hilbert Space Average Method on models like spin chains remain challenging. Thus, e.g. the transport properties of the Heisenberg chain is still ambiguous at the moment.

In face of the rapid miniaturization of many technical devices like e.g. com-

puter chips, and the trend to utilize of quantum mechanical systems, a deeper understanding of transport and relaxation processes and the thermodynamic properties of small systems will become necessary in the near future. At least, it will be important to know to what extent the long standing and successful thermodynamic concepts can be extended to the nanoscale and which new aspects should be taken into account. How small a system may be without loosing its thermodynamic behavior can be demonstrated by the fact that a driven single two level atom operate as a quantum thermodynamical machine: In those systems one finds a Carnot cycle of a heat engine or a heat pump. Besides the foundation of relaxation and transport on quantum mechanics also new aspects beyond a proper thermodynamical description are interesting. For example, there are some materials featuring extremely high thermal conductivities, due to magnetic excitations.

In conclusion we found that besides the emergence of equilibrium properties in small quantum systems, nonequilibrium thermodynamic aspects are already present far below the thermodynamic limit. Hopefully, the present work will help to shed new light on the fundamental aspects behind those interesting and long since known topics of relaxation and transport.

Part III.

Appendices

A. Hilbert Space Average of Expectation Values

In this Appendix we will evaluate the special trace expression of the Hilbert space averaged time evolution of an expectation value of the projection operator, defined in (6.46). In the following, we consider each order separately

$$\bar{S} = S_0 + S_1 + S_2 . \quad (\text{A.1})$$

Zeroth order: Using (6.5) and (6.6) the zeroth order of (6.46) yields

$$S_0 = \text{Tr}\{\hat{P}_{ij,a}\hat{P}_{i'j',a'}\} = \delta_{i'j}\delta_{j'i}\delta_{a'a}N_a . \quad (\text{A.2})$$

First order: By a cyclic rotation within the trace the first order refers to

$$\begin{aligned} S_1 &= \frac{i}{\hbar}\text{Tr}\{\hat{U}_1\hat{P}_{ij,a}\hat{P}_{i'j',a'} - \hat{P}_{i'j',a'}\hat{P}_{ij,a}\hat{U}_1\} \\ &= \frac{i}{\hbar}\delta_{a'a}(\delta_{i'j}\text{Tr}\{\hat{U}_1\hat{P}_{ij',a}\} - \delta_{j'i}\text{Tr}\{\hat{U}_1\hat{P}_{i'j,a}\}) , \end{aligned} \quad (\text{A.3})$$

where we have used (6.5) again. Concentrating on the first term, introducing the definition of the time evolution operator (6.26) and the interaction (6.21) one gets

$$\begin{aligned} \text{Tr}\{\hat{U}_1\hat{P}_{ij',a}\} &= \int_0^\tau d\tau' \text{Tr}\{\hat{V}(\tau')\hat{P}_{ij'}\hat{\Pi}_a\} \\ &= \int_0^\tau d\tau' \sum_{kl} \text{Tr}\{\hat{P}_{kl}\hat{C}_{kl}(\tau')\hat{P}_{ij'}\hat{\Pi}_a\} \\ &= \int_0^\tau d\tau' \sum_{kl} \text{Tr}_S\{\hat{P}_{kl}\hat{P}_{ij'}\} \text{Tr}_E\{\hat{C}_{kl}(\tau')\hat{\Pi}_a\} \\ &= \int_0^\tau d\tau' \text{Tr}_E\{\hat{C}_{j'i}(\tau')\hat{\Pi}_a\} . \end{aligned} \quad (\text{A.4})$$

Most of these terms are zero because of the projector to a respective band in the environment and thus an interaction causing a band-band transition

directly results into a zero trace. The rest is zero because of the two extra conditions for the interaction (6.15) and (6.16). We find an analogous result for the second trace of (A.3) and thus we finally end up with

$$S_1 = 0 . \quad (\text{A.5})$$

Second order: For the second order terms of (6.46) we get

$$S_2 = \frac{1}{\hbar^2} \text{Tr}\{\hat{U}_1 \hat{P}_{ij,a} \hat{U}_1 \hat{P}_{i'j',a'} - \delta_{ji'} \delta_{a'a} \hat{U}_2^\dagger \hat{P}_{ij',a'} - \delta_{j'i} \delta_{a'a} \hat{U}_2 \hat{P}_{i'j,a'}\} . \quad (\text{A.6})$$

Let us concentrate first on the last term, plugging in the definition of the time-evolution operator (6.27) and the interaction (6.21) we find

$$\begin{aligned} \text{Tr}\{\hat{U}_2 \hat{P}_{i'j,a'}\} &= \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}\{\hat{V}(\tau') \hat{V}(\tau'') \hat{P}_{i'j,a'}\} \\ &= \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \sum_m \text{Tr}_E\{\hat{C}_{jm}(\tau') \hat{C}_{mi'}(\tau'') \hat{\Pi}_{a'}\} . \end{aligned} \quad (\text{A.7})$$

Furthermore, plugging in the transformation into the interaction picture and using the fact that $[\hat{\Pi}_a, \hat{H}_E] = 0$, thus, swapping the whole time dependence to the first environmental operator by cyclic rotation of operators in the trace we find

$$\begin{aligned} &= \sum_m \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' e^{i\omega_{jm}\tau'} e^{i\omega_{mi'}\tau''} \\ &\quad \times \text{Tr}_E\{e^{\frac{i}{\hbar}\hat{H}_E\tau'} \hat{C}_{jm} e^{\frac{i}{\hbar}\hat{H}_E(\tau''-\tau')} \hat{C}_{mi'} e^{-\frac{i}{\hbar}\hat{H}_E\tau''} \hat{\Pi}_{a'}\} \\ &= \sum_m \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' e^{i(\omega_{jm}-\omega_{i'm})\tau''} \text{Tr}_E\{\hat{C}_{jm}(\tau' - \tau'') \hat{C}_{mi'} \hat{\Pi}_{a'}\} , \end{aligned} \quad (\text{A.8})$$

where we used the fact that $\omega_{ij} = -\omega_{ji}$ (cf. (6.19)). Since parts of the interaction are uncorrelated unless they are not adjoints of each other (see (6.14)) the above traces are only nonzero for the case $j = i'$. Doing the transformation $(\tau' - \tau'') \rightarrow \tau''$ we thus get

$$= \sum_m \delta_{i'j} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}_E\{\hat{C}_{jm}(\tau'') \hat{C}_{mj} \hat{\Pi}_{a'}\} . \quad (\text{A.9})$$

Finally, plugging in the unit operator of the environment in terms of projection operators, one finds

$$\begin{aligned} &= \sum_m \delta_{i'j} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}_E \{ \hat{C}_{jm}(\tau'') \sum_b \hat{\Pi}_b \hat{C}_{mj} \hat{\Pi}_{a'} \} \\ &= \sum_{mb} \delta_{i'j} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \text{Tr}_E \{ \hat{C}_{jm}(\tau'') \hat{\Pi}_b \hat{C}_{mj} \hat{\Pi}_{a'} \}. \end{aligned} \quad (\text{A.10})$$

Comparing this to (6.47) we end up with

$$\text{Tr} \{ \hat{U}_2 \hat{P}_{i'j,a'} \} = \frac{1}{2} \sum_{mb} \delta_{i'j} f_{jm,a'b}(\tau). \quad (\text{A.11})$$

Completely analogous we find for

$$\text{Tr} \{ \hat{U}_2^\dagger \hat{P}_{ij',a'} \} = \frac{1}{2} \sum_{mb} \delta_{j'i} f_{im,a'b}^*(\tau). \quad (\text{A.12})$$

It remains the computation of the first term of (A.6). Using the same argumentation as before (also the fact that there are no correlations between different parts of the interaction as well as a cyclic rotation within the trace operation) we find for the trace

$$\begin{aligned} &\text{Tr} \{ \hat{U}_1 \hat{P}_{ij,a} \hat{U}_1 \hat{P}_{i'j',a'} \} \\ &= \int_0^\tau d\tau' \int_0^\tau d\tau'' \delta_{ij} \delta_{i'j'} \text{Tr}_E \{ \hat{C}_{ii'}(\tau'') \hat{\Pi}_{a'} \hat{C}_{i'i}(\tau') \hat{\Pi}_a \}. \end{aligned} \quad (\text{A.13})$$

Again moving the time dependence τ' to the first operator we find

$$= \delta_{ij} \delta_{i'j'} \int_0^\tau d\tau' \int_0^\tau d\tau'' \text{Tr}_E \{ \hat{C}_{ii'}(\tau'' - \tau') \hat{\Pi}_{a'} \hat{C}_{i'i} \hat{\Pi}_a \}. \quad (\text{A.14})$$

Here, we integrate a function $g(\tau'' - \tau')$ over the square region $\{\{0, \tau\}, \{0, \tau\}\}$. Splitting up this integration into an integration over the lower respectively upper triangular region of the square, results into

$$\begin{aligned} I &= \int_0^\tau d\tau' \int_0^\tau d\tau'' g(\tau'' - \tau') \\ &= \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' g(\tau'' - \tau') + \int_0^\tau d\tau'' \int_0^{\tau''} d\tau' g(\tau'' - \tau'). \end{aligned} \quad (\text{A.15})$$

Exchanging $\tau' \rightleftharpoons \tau''$ in the second integration over the upper triangular region the integration results into

$$I = \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \left(g(\tau'' - \tau') + g(\tau' - \tau'') \right). \quad (\text{A.16})$$

Reintroducing the definition of the function g , shifting the time dependence of the operator in the second function to the other operator and expressing this trace expression by its adjoint, we get

$$I = \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' \left(\text{Tr}_E \{ \hat{C}_{ii'}(\tau'' - \tau') \hat{\Pi}_{a'} \hat{C}_{i'i} \hat{\Pi}_a \} + \text{Tr}_E \{ (\hat{C}_{ii'}(\tau'' - \tau') \hat{\Pi}_a \hat{C}_{i'i} \hat{\Pi}_a)^\dagger \} \right). \quad (\text{A.17})$$

Since the trace of an adjoint operator is the complex conjugate of the original trace, the integration simplifies to

$$I = 2\text{Re} \int_0^\tau d\tau' \int_0^{\tau'} d\tau'' g(\tau' - \tau''). \quad (\text{A.18})$$

Using this insight in (A.14) we can identify again the integration with the environmental correlation function (6.47)

$$\text{Tr} \{ \hat{U}_1 \hat{P}_{ij,a} \hat{U}_1 \hat{P}_{i'j',a'} \} = \delta_{ij} \delta_{i'j'} \text{Re} f_{ii',aa'}(\tau). \quad (\text{A.19})$$

Putting together eqs. (A.11), (A.12) and (A.19) we get the complete second order of the important trace in (A.1)

$$S_2 = \frac{1}{\hbar^2} \left(\delta_{ij} \delta_{i'j'} \text{Re} f_{ii',aa'}(\tau) - \frac{1}{2} \sum_{mb} \delta_{j'i} \delta_{ji'} \delta_{a'a} [f_{im,a'b}(\tau) + f_{jm,a'b}^*(\tau)] \right) \quad (\text{A.20})$$

Thus, plugging in the zeroth order (A.2) the first order (A.5) the second order terms (A.20) into (A.1) one gets the final result for the trace expression in (6.45).

B. Hyperspheres

In the following we consider a n -dimensional Cartesian space with the coordinates $\{x_1, \dots, x_n\}$. Within this space a d dimensional hypersphere with radius R is introduced by

$$\text{sph}(d) : \sum_{i=1}^d x_i^2 = R^2 , \quad (\text{B.1})$$

where we have sorted the coordinates according to the coordinates of the hypersphere.

B.1. Surface of a Hypersphere

We restrict ourselves to a hypersphere with radius $R = 1$. To evaluate its surface $\mathcal{O}(R = 1, d)$, we consider the special integral

$$I(d) = \int_{\mathbb{R}^d} e^{-\sum_{i=1}^d x_i^2} \prod_{i=1}^d dx_i = \prod_{i=1}^d \int_{-\infty}^{\infty} e^{-x_i^2} dx_i = \pi^{\frac{d}{2}} . \quad (\text{B.2})$$

Generalized spherical coordinates in the d dimensional subspace are defined by the transformation $\{x_1, \dots, x_d\} \mapsto \{r, \phi_1, \dots, \phi_{d-1}\}$

$$\begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_j \\ \vdots \\ x_{d-1} \\ x_d \end{pmatrix} = \begin{pmatrix} r \cos \phi_1 \\ r \sin(\phi_1) \cos(\phi_2) \\ \vdots \\ r \prod_{i=1}^{j-1} \sin(\phi_i) \cos(\phi_j) \\ \vdots \\ r \prod_{i=1}^{d-2} \sin(\phi_i) \cos(\phi_{d-1}) \\ r \prod_{i=1}^{d-2} \sin(\phi_i) \sin(\phi_{d-1}) \end{pmatrix} , \quad (\text{B.3})$$

and the Jacobian matrix (functional matrix)

$$\mathbf{F} = \begin{pmatrix} \frac{\partial x_1}{\partial r} & \frac{\partial x_1}{\partial \phi_1} & \cdots & \frac{\partial x_1}{\partial \phi_{d-1}} \\ \frac{\partial x_2}{\partial r} & \frac{\partial x_2}{\partial \phi_1} & \cdots & \frac{\partial x_2}{\partial \phi_{d-1}} \\ \vdots & \ddots & & \vdots \\ \frac{\partial x_d}{\partial r} & \frac{\partial x_d}{\partial \phi_1} & \cdots & \frac{\partial x_d}{\partial \phi_{d-1}} \end{pmatrix}. \quad (\text{B.4})$$

The determinant of this matrix can be evaluated and reads

$$\det \mathbf{F} = r^{d-1} \sin^{d-2}(\phi_1) \sin^{d-3}(\phi_2) \cdots \sin(\phi_{d-2}). \quad (\text{B.5})$$

The volume element transforms according to

$$\begin{aligned} \prod_{i=1}^d dx_i &= |\det \mathbf{F}| dr \prod_{i=1}^{d-1} d\phi_i \\ &= r^{d-1} dr \sin^{d-2}(\phi_1) d\phi_1 \cdots \sin(\phi_{d-2}) d\phi_{d-2} d\phi_{d-1} \\ &= r^{d-1} dr d\Omega. \end{aligned} \quad (\text{B.6})$$

Now we evaluate the integral in spherical coordinates, too,

$$I(d) = \int_0^\infty e^{-r^2} r^{d-1} dr \int d\Omega. \quad (\text{B.7})$$

The last integration is just the surface $\mathcal{O}(1, d)$ of the hypersphere, and we find by evaluating the first one

$$I(d) = \frac{\Gamma(\frac{d}{2})}{2} \mathcal{O}(1, d). \quad (\text{B.8})$$

Thus, the surface of the hypersphere with radius $R = 1$ is

$$\mathcal{O}(1, d) = \frac{2I(d)}{\Gamma(\frac{d}{2})} = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})}. \quad (\text{B.9})$$

If we evaluate the surface of a hypersphere with radius R , we have to renormalize the exponent in (B.2) by $1/R^2$, finding $I(d) = \pi^{d/2} R^d$. Additionally, replacing the radius variable of the generalized spherical coordinate $r \mapsto r/R$ and integrating (B.7), we find

$$I(d) = \frac{1}{2} R \Gamma(d/2) \mathcal{O}(R, d), \quad (\text{B.10})$$

and thus

$$\mathcal{O}(R, d) = \frac{2\pi^{\frac{d}{2}}}{\Gamma(d/2)} R^{d-1}. \quad (\text{B.11})$$

B.2. Integration of a Function on a Hypersphere

To integrate a polynomial function over the hypersphere surface one can use the same approach as in the last Section. Consider the function

$$f(x_i, x_j) = (x_i)^l (x_j)^k \quad \text{with } l, k \geq 0 , \quad (\text{B.12})$$

and the integration

$$\begin{aligned} I(d) &= \int_{\mathbb{R}^d} f(x_i, x_j) \exp\left(-\frac{1}{R^2} \sum_{i'=1}^d x_{i'}^2\right) \prod_{j'} dx_{j'} \\ &= \int_{\mathbb{R}^d} (x_i)^l (x_j)^k \exp\left(-\frac{1}{R^2} \sum_{i'=1}^d x_{i'}^2\right) \prod_{j'} dx_{j'} \\ &= \pi^{\frac{d-2}{2}} R^{d-2} \int_{-\infty}^{\infty} (x_i)^l \exp\left(-\frac{x_i^2}{R^2}\right) dx_i \int_{-\infty}^{\infty} (x_j)^k \exp\left(-\frac{x_j^2}{R^2}\right) dx_j \\ &= \pi^{\frac{d-2}{2}} \frac{1}{4} (1 + (-1)^l) \Gamma\left(\frac{l+1}{2}\right) (1 + (-1)^k) \Gamma\left(\frac{k+1}{2}\right) R^{d+l+k} . \end{aligned} \quad (\text{B.13})$$

We switch to generalized spherical coordinates, as in the previous section, which transforms the function (B.12) into

$$\begin{aligned} f(x_i, x_j) &\mapsto f\left(\left\{\frac{r}{R}, \phi_1, \dots, \phi_{d-1}\right\}\right) \\ &= \left(\frac{r}{R} \prod_{i'=1}^{i-1} \sin \phi_{i'} \cos \phi_i\right)^l \left(\frac{r}{R} \prod_{i'=1}^{j-1} \sin \phi_{i'} \cos \phi_j\right)^k \\ &= \left(\frac{r}{R}\right)^l \left(\frac{r}{R}\right)^k (z_i(\{\phi_{i'}\}))^l (z_j(\{\phi_{i'}\}))^k , \end{aligned} \quad (\text{B.14})$$

and the integral into

$$I(d) = \int_0^\infty e^{-\frac{r^2}{R^2}} \left(\frac{r}{R}\right)^{d+l+k-1} dr \int (z_i(\{\phi_{i'}\}))^l (z_j(\{\phi_{i'}\}))^k d\Omega . \quad (\text{B.15})$$

Here we are interested in the last integral, $Z(R, d, l, k)$. From

$$I(d) = \frac{R\Gamma(\frac{d+l+k}{2})}{2} Z(1, d, l, k) \quad (\text{B.16})$$

we find

$$\begin{aligned} Z(R, d, l, k) &= \frac{2I(d)}{R\Gamma(\frac{d+l+k}{2})} \\ &= \frac{\pi^{\frac{d-2}{2}}}{2}(1+(-1)^l)(1+(-1)^k)\frac{\Gamma(\frac{l+1}{2})\Gamma(\frac{k+1}{2})}{\Gamma(\frac{d+l+k}{2})}R^{d+l+k-1}. \end{aligned} \quad (\text{B.17})$$

Note that $Z(R, d, 0, 0) = \mathcal{O}(R, d)$ and that all integrals are zero, if either l or k is odd. We need some special and normalized integrals only

$$\mathcal{O}(R, d, l, k) := \frac{Z(R, d, l, k)}{Z(R, d, 0, 0)}, \quad (\text{B.18})$$

$$\mathcal{O}(R, d, 0, 1) = \mathcal{O}(R, d, 1, 1) = 0, \quad (\text{B.19})$$

$$\mathcal{O}(R, d, 0, 2) = \frac{R^2}{d}, \quad (\text{B.20})$$

$$\mathcal{O}(R, d, 2, 2) = \frac{R^4}{d^2 + 2d}, \quad (\text{B.21})$$

$$\mathcal{O}(R, d, 0, 4) = \frac{3R^4}{d^2 + 2d}. \quad (\text{B.22})$$

C. Hilbert Space Averages

In this Appendix we calculate the concrete Hilbert space average of the special quantities needed for the Hilbert Space Average Method introduced in Chap. 6 and used especially in Chap. 15. We will use some techniques introduced in the App. B, e.g. the integration of polynomial functions over a hypersphere in a high dimensional space. For the general definition of Hilbert space averages see [40].

C.1. Definition

Let us consider an n dimensional Hilbert space and the general state $|\psi\rangle$ within this space. The overall normalization condition for the state defines a hypersphere in the $2n$ dimensional parameter space of real and imaginary part $\{\eta_i, \xi_i\}$ of the complex amplitude ψ_i of the state vector

$$\text{sph}(2n) : \sum_i (\eta_i^2 + \xi_i^2) = \langle \psi | \psi \rangle = 1 . \quad (\text{C.1})$$

This side condition defines the region in the high dimensional space to which the dynamics is restricted. Furthermore, there could be some more side conditions, e.g. the total energy conservation, which also restrict the trajectory of the system to a small subspace of the total Hilbert space. This subspace is often called accessible region (AR).

Let f be a function of the complete state $|\psi\rangle$ of the system in the accessible region, AR, of the whole Hilbert space. The Hilbert space is represented by a $2n$ -dimensional Cartesian space, in which the Hilbert space average over AR of f is defined as

$$[\![f]\!] = \frac{\int_{\text{AR}} f(\{\eta_i, \xi_i\}) \prod_{i=1}^n d\eta_i d\xi_i}{\int_{\text{AR}} \prod_{i=1}^n d\eta_i d\xi_i} , \quad (\text{C.2})$$

where the integral in the denominator is just the area $\mathcal{O}(\text{AR})$ of the accessible region we are integrating over. The Hilbert space average meets all properties

of standard averages

$$\llbracket c f \rrbracket = c \llbracket f \rrbracket \quad \text{with} \quad c \in \mathbb{C}, \quad (\text{C.3})$$

$$\llbracket f + f' \rrbracket = \llbracket f \rrbracket + \llbracket f' \rrbracket, \quad (\text{C.4})$$

$$\llbracket f^* \rrbracket = \llbracket f \rrbracket^*. \quad (\text{C.5})$$

C.2. Hilbert Space Average of Expectation Values

In order to calculate the Hilbert space average of an expectation value of a Hermitian operator $\langle \psi | \hat{A} | \psi \rangle$, it is useful to consider this quantity in explicit tensor notation

$$\llbracket \langle \psi | \hat{A} | \psi \rangle \rrbracket = \llbracket \sum_{ij} \psi_i^* A_{ij} \psi_j \rrbracket = \sum_{ij} A_{ij} \llbracket \psi_i^* \psi_j \rrbracket. \quad (\text{C.6})$$

The last expression is just an integral of a polynomial function in parameter space over the hypersphere with radius 1. Such integrals over coordinates are certainly zero, if we integrate over a single linear coordinate (c.f. App. B.2). Therefore this sum has non zero addends for $i = j$ only, implying for the Hilbert space average

$$\llbracket \psi_i^* \psi_i \rrbracket = \frac{\int_{\text{AR}} |\psi_i|^2 \prod_n d\eta_i d\xi_i}{\int_{\text{AR}} \prod_n d\eta_i d\xi_i}, \quad (\text{C.7})$$

where AR denotes the accessible region for the system under some side conditions as, e.g., the overall energy conservation. The integral in the denominator is just the surface area of the respective hypersphere $Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)$

$$= \frac{\int_{\text{AR}} (\eta_i^2 + \xi_i^2) \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)}. \quad (\text{C.8})$$

With App. B.2 and especially (B.20) we find eventually

$$= \frac{2Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 2, 0)}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} = \frac{\langle \psi | \psi \rangle}{n}. \quad (\text{C.9})$$

The Hilbert space average of the expectation value now reads

$$\llbracket \langle \psi | \hat{A} | \psi \rangle \rrbracket = \sum_{ij} A_{ij} \frac{\langle \psi | \psi \rangle}{n} \delta_{ij} = \frac{\langle \psi | \psi \rangle}{n} \sum_i A_{ii} = \frac{\langle \psi | \psi \rangle}{n} \text{Tr}\{\hat{A}\}, \quad (\text{C.10})$$

and, because of $\langle \psi | \psi \rangle = 1$, especially

$$\llbracket \langle \psi | \hat{A} | \psi \rangle \rrbracket = \frac{\text{Tr}\{\hat{A}\}}{n}. \quad (\text{C.11})$$

C.3. Special Hilbert-Space Averages

In case the total wave vector is given by $|\psi\rangle = |\psi^{(1)}\rangle + |\psi^{(2)}\rangle$ a decomposition into two totally independent subspaces with

$$\langle \psi | \psi \rangle = \langle \psi^{(1)} | \psi^{(1)} \rangle + \langle \psi^{(2)} | \psi^{(2)} \rangle = 1 . \quad (\text{C.12})$$

According to this normalization condition, it is again possible to formulate a hypersphere subsidiary condition in each subspace, subspace 1 with dimension n_1 as well as subspace 2 with the dimension n_2 ,

$$\text{sph}(2n_1) : \sum_i (\eta_i^{(1)})^2 + (\xi_i^{(1)})^2 = \langle \psi^{(1)} | \psi^{(1)} \rangle = 1 - \langle \psi^{(2)} | \psi^{(2)} \rangle , \quad (\text{C.13})$$

$$\text{sph}(2n_2) : \sum_j (\eta_j^{(2)})^2 + (\xi_j^{(2)})^2 = \langle \psi^{(2)} | \psi^{(2)} \rangle . \quad (\text{C.14})$$

These are two hyperspheres with the radii $\sqrt{\langle \psi^{(1)} | \psi^{(1)} \rangle}$ and $\sqrt{\langle \psi^{(2)} | \psi^{(2)} \rangle}$, respectively. The index i is restricted to the subspace 1 with $2n_1$ coordinates ($\{\eta_i^{(1)}, \xi_i^{(1)}\}$), whereas j belongs to the other subspace 2 with $2n_2$ coordinates ($\{\eta_j^{(2)}, \xi_j^{(2)}\}$).

Let us calculate the Hilbert space average of $\llbracket \langle \psi^{(1)} | \hat{A} | \psi^{(2)} \rangle \rrbracket$ with an arbitrary operator \hat{A} by writing it out in detailed tensor notation

$$\llbracket \langle \psi^{(1)} | \hat{A} | \psi^{(2)} \rangle \rrbracket = \llbracket \sum_{ij} (\psi_i^{(1)})^* A_{ij} \psi_j^{(2)} \rrbracket = \sum_{ij} A_{ij} \llbracket (\psi_i^{(1)})^* \psi_j^{(2)} \rrbracket . \quad (\text{C.15})$$

Since $|\psi^{(1)}\rangle$, $|\psi^{(2)}\rangle$ refer to entirely different subspaces, the $\psi_i^{(1)}$ and $\psi_j^{(2)}$ always consist of different coordinates, and we get for the Hilbert space average, as argued in App. B.2

$$\llbracket (\psi_i^{(1)})^* \psi_j^{(2)} \rrbracket = \frac{\int_{\text{AR}} (\psi_i^{(1)})^* \prod_n d\eta_n^{(1)} d\xi_n^{(1)} \int_{\text{AR}} \psi_j^{(2)} \prod_m d\eta_m^{(2)} d\xi_m^{(2)}}{\int_{\text{AR}} \prod_n d\eta_n^{(1)} d\xi_n^{(1)} \prod_m d\eta_m^{(2)} d\xi_m^{(2)}} = 0 . \quad (\text{C.16})$$

Thus we get for the complete Hilbert space average

$$\llbracket \langle \psi^{(1)} | \hat{A} | \psi^{(2)} \rangle \rrbracket = 0 . \quad (\text{C.17})$$

Of course, the Hilbert space average of the adjoint is zero as well.

For the Hilbert space average of $\llbracket \langle \psi^{(1)} | \hat{A} | \psi^{(1)} \rangle \rrbracket$ we can use the general result (C.11), because it is just the Hilbert space average of an expectation value

of a Hermitian operator. Note that $|\psi^{(1)}\rangle$ is not normalized and refers to the subspace 1. It follows that the trace does not run over the whole space but over the subspace 1 only, finding

$$\llbracket \langle \psi^{(1)} | \hat{A} | \psi^{(1)} \rangle \rrbracket = \frac{\langle \psi^{(1)} | \psi^{(1)} \rangle}{n_1} \text{Tr}_1\{\hat{A}\}. \quad (\text{C.18})$$

D. Hilbert-Space Variance

Turning to the Hilbert space variance of the expectation value of a Hermitian operator \hat{A} (n dimension of the Hilbert space),

$$\Delta_H = \sqrt{\llbracket (\langle \psi | \hat{A} | \psi \rangle)^2 \rrbracket - \llbracket \langle \psi | \hat{A} | \psi \rangle \rrbracket^2}, \quad (D.1)$$

we consider in tensor notation

$$\llbracket (\langle \psi | \hat{A} | \psi \rangle)^2 \rrbracket = \llbracket \langle \psi | \hat{A} | \psi \rangle \langle \psi | \hat{A} | \psi \rangle \rrbracket = \sum_{ijkl} A_{ij} A_{kl} \llbracket \psi_i^* \psi_j \psi_k^* \psi_l \rrbracket. \quad (D.2)$$

In case of $i \neq j \neq k \neq l$ all addends of the sum are zero, and also, if three of the four indices are equal (see App. B.2). Only if all indices are equal or if there are always pairs of two equal indices, the addend may be nonzero. Collecting all possible nonzero terms we get

$$\begin{aligned} \llbracket (\langle \psi | \hat{A} | \psi \rangle)^2 \rrbracket &= \sum_{\substack{ij \\ i \neq j}} \llbracket |\psi_i|^2 |\psi_j|^2 \rrbracket (A_{ii} A_{jj} + A_{ij} A_{ji}) \\ &\quad + \sum_{\substack{ij \\ i \neq j}} \llbracket (\psi_i^*)^2 (\psi_j)^2 \rrbracket A_{ij} A_{ij} + \sum_i A_{ii}^2 \llbracket |\psi_i|^4 \rrbracket. \end{aligned} \quad (D.3)$$

In the following we calculate the three remaining Hilbert space averages: The first one reads ($i \neq j$)

$$\begin{aligned} \llbracket |\psi_i|^2 |\psi_j|^2 \rrbracket &= \frac{\int_{\text{AR}} |\psi_i|^2 |\psi_j|^2 \prod_n d\eta_i d\xi_i}{\int_{\text{AR}} \prod_n d\eta_i d\xi_i} = \frac{\int_{\text{AR}} |\psi_i|^2 |\psi_j|^2 \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} \\ &= \frac{4Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 2, 2)}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} = \frac{1}{n(n+1)}. \end{aligned} \quad (D.4)$$

The second one is a little bit more complicated, we have to look for the expression in the coordinates ($i \neq j$)

$$\begin{aligned} \llbracket (\psi_i^*)^2 (\psi_j)^2 \rrbracket &= \frac{\int_{\text{AR}} (\psi_i^*)^2 (\psi_j)^2 \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} \\ &= \frac{\int_{\text{AR}} \eta_i^2 \eta_j^2 - \eta_i^2 \xi_j^2 - \xi_i^2 \eta_j^2 + \xi_i^2 \xi_j^2 \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} \\ &\quad + \frac{\int_{\text{AR}} 2i\eta_i \xi_i (\xi_j^2 - \eta_j^2) + 2i\eta_j \xi_j (\eta_i^2 - \xi_i^2) \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)}. \end{aligned} \quad (\text{D.5})$$

The last two integrals are zero because of the linear coordinates. Since the first integrals feature the same value but different signs, we get

$$\llbracket (\psi_i^*)^2 (\psi_j)^2 \rrbracket = 0. \quad (\text{D.6})$$

The remaining Hilbert space average reads

$$\begin{aligned} \llbracket |\psi_i|^4 \rrbracket &= \frac{\int_{\text{AR}} |\psi_i|^4 \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} = \frac{\int_{\text{AR}} \eta_i^4 + \xi_i^4 + 2\eta_i^2 \xi_i^2 \prod_n d\eta_i d\xi_i}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} \\ &= \frac{2Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 4, 0)}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} + \frac{2Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 2, 2)}{Z(\sqrt{\langle \psi | \psi \rangle}, 2n, 0, 0)} = \frac{2}{n(n+1)}. \end{aligned} \quad (\text{D.7})$$

All together we find

$$\llbracket (\langle \psi | \hat{A} | \psi \rangle)^2 \rrbracket = \frac{1}{n(n+1)} \left(\sum_{\substack{ij \\ i \neq j}} (A_{ii} A_{jj} + A_{ij} A_{ji}) + 2 \sum_i A_{ii}^2 \llbracket |\psi_i|^4 \rrbracket \right). \quad (\text{D.8})$$

The missing terms in the first two sums can be found in the last one

$$\begin{aligned} \llbracket (\langle \psi | \hat{A} | \psi \rangle)^2 \rrbracket &= \frac{1}{n(n+1)} \sum_{ij} (A_{ii} A_{jj} + A_{ij} A_{ji}) \\ &= \frac{1}{n(n+1)} (\text{Tr}\{\hat{A}\}^2 + \text{Tr}\{\hat{A}^2\}). \end{aligned} \quad (\text{D.9})$$

With this result and the Hilbert space average of the expectation value we can now calculate the Hilbert space variance of the expectation value

$$\Delta_H = \frac{1}{n+1} \left[\frac{\text{Tr}\{\hat{A}^2\}}{n} - \left(\frac{\text{Tr}\{\hat{A}\}}{n} \right)^2 \right] \quad (\text{D.10})$$

thus, the Hilbert space variance squared is just the spectral variance squared, divided by the dimension plus 1.

E. German Summary – Deutsche Zusammenfassung

Das ist so die Art der Natur: Sie übt sich
an kleinen Dingen und bietet im Geringsten
Beispiele für Gewaltiges.

Lucius Annaeus Seneca [139]

Die phänomenologische Thermodynamik und die Statistische Mechanik ist wohl eine der weitreichendsten Theorien der modernen Physik. Ihr Einfluss reicht von den wichtigsten technischen Errungenschaften unserer modernen Gesellschaft, wie Motoren, Kühlschränken und Computern bis zu neuesten physikalischen Erkenntnissen, beispielsweise Bose-Einstein Kondensaten, Supraleitern oder Schwarzen Löchern. Neben den technischen Anwendungen, die hauptsächlich zum Ruhm dieser einzigartigen Theorien beigetragen haben, ist vor allem eine Frage für viele Physiker wichtig gewesen: Wie kann es zu dem in der Thermodynamik postulierten irreversiblen Verhalten kommen, nachdem doch die meisten thermodynamischen Systeme mikroskopisch betrachtet einer reversiblen Theorie folgen? So berühmte Physiker wie Boltzmann [7], Birkhoff [5], Ehrenfest [25], Gibbs [43] und von Neumann [110] versuchten, unter Zuhilfenahme diverser zusätzlicher Annahmen (z.B. Ergodenhypothese), die Thermodynamik auf die klassische Hamiltonsche Mechanik aufzubauen. Trotz des scheinbar alltäglichen Auftretens irreversiblen Verhaltens konnten diese zusätzlichen Annahmen leider nur für einzelne ausgezeichnete Systeme bewiesen werden.

Kürzlich ist es nun gelungen die Thermodynamik vollständig auf die Quantenmechanik aufzubauen [40]. Natürlich ist auch die Quantenmechanik genau wie die klassische Mechanik eine reversible Theorie, die allerdings einige Eigenschaften birgt, die es klassisch nicht gibt. Es stellte sich heraus, dass vor allem die Verschränkung zwischen System und Umgebung zu lokal irreversiblem Verhalten führt, ohne Zuhilfenahme sonstiger Annahmen. Neben der Emergenz thermodynamischen Verhaltens aus der Quantenmechanik und der daraus resultierenden Fundierung der Thermostatistik, bietet dieser neue Zugang des Weiteren die Chance auch sehr kleine Quantensysteme unter thermodynamischen Bedingungen untersuchen zu können.

schem Blickwinkel zu betrachten. Dies ist von zentraler Bedeutung in einer Zeit, in der mit fortschreitender Miniaturisierung die Grenzen von klassischer und quanten Welt immer weiter ausgelotet werden.

Nachdem das Erreichen des Gleichgewichts innerhalb der *Quantenthermodynamik* erklärbar wurde, stellt sich im Weiteren natürlich die Frage nach verschiedenen Phänomenen nahe am Gleichgewicht, wie beispielsweise dem Zerfall ins Gleichgewicht oder dem Transport von Wärme, und deren Erklärung aus der Quantenmechanik. Diesen Fragestellungen ist die vorliegende Arbeit gewidmet. Es wird versucht diese weiterführende Thematik durch Erweiterung der in der Gleichgewichtsquantenthermodynamik erarbeiteten Konzepte zu bearbeiten. Der Vergleich mit herkömmlichen Methoden wie beispielsweise der Theorie offener Quantensysteme soll zu einer Einordnung der neuen Betrachtungsweise beitragen. Die Arbeit gliedert sich in zwei Teile, zunächst die Betrachtung des Zerfalls in der Quantenmechanik und dann die Untersuchung von Wärmeleitung.

E.1. Zerfall ins Gleichgewicht

Eine typische thermodynamische Situation ist gekennzeichnet durch die Zweiteilung der „Welt“ in ein System, das von irgendeinem Interesse für den Beobachter ist, und den Rest, das so genannte Reservoir oder einfach die Umgebung. Insgesamt haben wir es so mit einem hochdimensionalen Quantensystem zu tun, bei dem wir uns allerdings nur für die Zeitentwicklung eines recht kleinen Teils interessieren. Da im Allgemeinen die vollständige Dynamik nicht oder nur unter unzumutbarem Aufwand zugänglich ist, wird oft versucht durch Näherungen eine geschlossene reduzierte dynamische Gleichung für den interessanten Teil herzuleiten. Eine sehr bekannte Methode in diesem Kontext ist die *Quantenmastergleichung*, die in der Theorie *offener Quantensysteme* Verwendung findet und für unendlich große Systeme entwickelt wurde. Daneben steht eine recht junge Theorie, die *Hilbertraummittelmethode*, die auch für endliche bzw. sogar sehr kleine Systeme anwendbar bleibt. Im Folgenden soll auf die zentralen Aspekte hinter diesen Methoden eingegangen werden und dieselben zur Untersuchung des Zerfalls ins Gleichgewicht verwendet werden.

E.1.1. Offene Quantensysteme

Innerhalb der Theorie offener Quantensysteme kann die Wirkung der Umgebung auf das System durch Dissipatoren beschrieben werden, die nur im Unterraum des Systems agieren. Das bedeutet, dass geschlossene dynamische Gleichungen für das System angegeben werden können ohne explizit Freiheits-

grade des Reservoirs zu berücksichtigen (Quantenmastergleichung). So gehen nur Parameter wie Badtemperatur und Kopplungsstärke des Bades an das System in die dynamische Beschreibung ein. Die Herleitung der entsprechenden Gleichungen mittels der Methode nach Nakajima und Zwanzig (siehe z.B. [13]), verlässt sich dabei auf eine Reihe von Näherungen: die Born-, Markov-, Redfield-, und RWA-Näherung (RWA: rotating wave approximation).

Nach der „Einschwingphase“ relaxiert das gesamte System ad definitionem in einen thermischen Gleichgewichtszustand. Interessante Fragen stellen sich, wenn das System selbst kein einzelnes Teilchen ist, sondern aus einer Anzahl schwach gekoppelter Untereinheiten besteht (topologische Struktur im Ortsraum). Bei Ankopplung der Umgebung ausschließlich an den Rand des Systems (z.B. Badkopplung an eine Spinkette, aber nur an einen der Endspins) stellt man fest, dass für schwach gekoppelte Systeme auch jedes einzelne System in einen thermischen Gleichgewichtszustand relaxiert, entsprechend der Temperatur des Bades. Für stärker gekoppelte Systeme ist dies nicht mehr der Fall. Einzelne Untereinheiten können durchaus höhere oder tiefere Temperaturen haben. Des Weiteren ist thermodynamisches bzw. statistisches Relaxationsverhalten im allgemeinen durch einen exponentiellen Zerfall in das globale Gleichgewicht charakterisiert. Der angesprochene Relaxationsprozess jedoch ist alles andere als solch ein exponentieller Zerfall.

Die hier verwendete Theorie offener Quantensysteme beschreibt die Kopplung eines Systems an eine unendlich große Umgebung. Innerhalb der Quantenthermodynamik interessieren wir uns jedoch insbesondere für das Auftreten thermodynamischen Verhaltens in kleinen endlichdimensionalen Systemen, also auch für die Einbettung in endliche Umgebungen. Für die Kopplung an endliche Bäder jedoch bestehen einige Zweifel an der Richtigkeit der angesprochenen Näherungen, die zur Herleitung der Quantenmastergleichung nötig sind [12]. Aus diesem Grund wird im Folgenden eine neue Theorie eingeführt um den Zerfall von Systemen gekoppelt an endliche Umgebungen näher zu untersuchen.

E.1.2. Hilbertraummittelmethode

Betrachtet wird das in Abb. E.1 gezeigte Modellsystem, ein Zweiniveausystem gekoppelt an eine Umgebung bestehend aus zwei Bändern gleicher Breite, in denen eine eventuell unterschiedliche Anzahl von Niveaus gleichverteilt angeordnet sind. Die Wechselwirkung zwischen den beiden Teilen soll den Energieaustausch erlauben, kann aber auch nicht energieaustauschende Terme enthalten, d.h. Anteile die nur Verschränkung aufbauen.

Um die zeitabhängige Wahrscheinlichkeit, das System in einem seiner Energieeigenzustände zu finden, ausrechnen zu können, benötigt man die Zeitent-

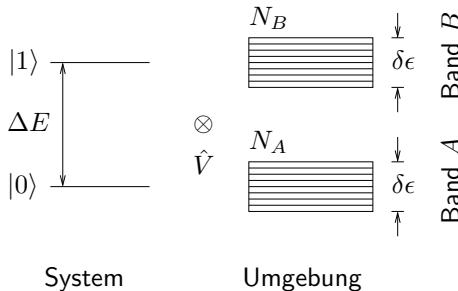


Abbildung E.1.: Zwei Niveau System gekoppelt (\hat{V}) an ein endliches Bad mit zwei Bändern der breite $\delta\epsilon$, die N_A bzw. N_B Niveaus enthalten.

wicklung des Zustands des Gesamtsystems $|\psi(t)\rangle$). Definiert man einen Projektor \hat{P}_i auf einen Subraum des Hilbertraums, z.B. System oben und Bad in einer beliebigen Superposition der Zustände im unteren Band, ist die Wahrscheinlichkeit das Gesamtsystem in diesem Subraum zu finden gegeben durch

$$P_i(t) = \langle \psi(t) | \hat{P}_i | \psi(t) \rangle. \quad (\text{E.1})$$

Die Zeitentwicklung des Zustands ist gegeben durch die Schrödingergleichung des Gesamtsystems, eines hochdimensionalen linearen Differentialgleichungssystems und damit schwierig zu lösen. Weit besser wäre eine dynamische Gleichung für das System alleine ohne die Umgebung explizit mitzunehmen. Aus diesem Grund betrachtet man die Kurzzeitentwicklung

$$P_i(\tau) = \langle \psi(\tau) | \hat{P}_i | \psi(\tau) \rangle = \langle \psi(0) | \hat{D}^\dagger(\tau) \hat{P}_i \hat{D}(\tau) | \psi(0) \rangle, \quad (\text{E.2})$$

wobei der Operator \hat{D} eine übliche Dyson-Zeitentwicklung darstellt, der für kurze Zeiten und schwache Kopplung in zweiter Ordnung Störungstheorie betrachtet werden kann.

Die Zeitentwicklung des Erwartungswerts ist ein ziemlich komplizierter Ausdruck dessen Wert nicht unmittelbar analytisch zugänglich ist. Deshalb mittelt man diesen Erwartungswert über alle zugänglichen Zustände des Hilbertraums unter Berücksichtigung der durch den Anfangszustand vorgegebenen Beschränkungen und ersetzt den komplizierten exakten Ausdruck durch dessen *Hilbertraummittelwert*

$$P_i(\tau) = \langle \psi(0) | \hat{D}^\dagger(\tau) \hat{P}_i \hat{D}(\tau) | \psi(0) \rangle \approx \llbracket \langle \psi | \hat{D}^\dagger(\tau) \hat{P}_i \hat{D}(\tau) | \psi \rangle \rrbracket. \quad (\text{E.3})$$

In voller Allgemeinheit ist das Ergebnis dieser Betrachtung zunächst eine geschlossene dynamische Gleichung für die Zeitentwicklung der Wahrscheinlichkeiten bestimmte Bänder im Gesamtsystem zu besetzen. Für das in Abb. E.1

gezeigte einfache Modellsystem unter festgelegten Anfangsbedingungen ist es des Weiteren möglich eine geschlossene dynamische Gleichung für die reduzierte Dichtematrix des Systems alleine abzuleiten. Außerdem lassen sich Modellkriterien angeben, unter denen der Zerfall eines Systems tatsächlich entsprechend dieser dynamischen Gleichungen verläuft. Sind alle Voraussetzung für die Anwendbarkeit der durchgeföhrten Näherungen erfüllt, kann tatsächlich ein exponentieller Zerfall hin in den von der Quantenthermodynamik vorhergesagten Gleichgewichtszustand gefunden werden. Dieses theoretische Ergebnis wird gestützt durch die Beobachtung des Zerfalls in kleinen Modellsystemen mit nur einigen hundert Energieniveaus innerhalb reiner Schrödingerdynamik.

Neben dem Erreichen einer thermischen Verteilung im System (Diagonalelemente der Dichtematrix), kann auch das Verschwinden von Kohärenzen, also der Zerfall von Nichtdiagonalelementen der Dichtematrix, untersucht werden. Bei nur energieaustauschenden Wechselwirkungen ist die Dekohärenzzeit T_2 strikt an die Thermalisierungszeit T_1 gekoppelt ($T_2 = 2T_1$). Enthält die Koppelung jedoch nichtenergieaustauschende Terme (Verschränkungsterme), wird die Dekohärenzzeit im Vergleich zur Thermalisierungszeit stark reduziert. Dieses Ergebnis entspricht vollständig der Erwartung bei entsprechenden Zerfallsprozessen in der Quantenmechanik [154].

Zusammenfassend lässt sich sagen, dass es tatsächlich möglich ist auch in endlichen Badkopplungsszenarien und sehr kleinen Quantensystemen einen regulären Zerfall ins Gleichgewicht zu beobachten. Vielleicht wird es in Zukunft möglich sein auch experimentell den Zerfall eines kleinen Quantensystems (z.B. Spins) gekoppelt an ein einzelnes Moleköl oder einen einzelnen Quantenpunkt zu beobachten.

E.2. Transport

Vor zweihundert Jahren fand Fourier [33] durch Experimente und theoretische Überlegungen heraus, dass Wärme oder wie wir heute wissen Energie diffusiv durch einen Festkörper transportiert wird. Sein berühmtes Gesetz verknüpft den Wärmestrom \mathbf{J} durch ein Material mit dem internen Temperaturgradienten ∇T ,

$$\mathbf{J} = -\kappa \nabla T, \quad (\text{E.4})$$

vermittels der Materialkonstante κ (Wärmeleitfähigkeit).

Das Ziel vieler folgender wissenschaftlicher Untersuchungen war die mikroskopische Begründung dieses phänomenologischen Gesetzes auf der Basis der klassischen Mechanik. Zunächst versuchte Debye [22, 77] die Wärmeleitung in Isolatoren mit Hilfe der kinetischen Gastheorie der Phononen im Festkörper

zu beschreiben. Peierls [113–115] erweiterte diesen Ansatz durch die Formulierung einer Boltzmann Gleichung für das Phononengas. Damit wurde es möglich viele Eigenschaften der Wärmeleitfähigkeit von Isolatoren zufriedenstellend zu erklären. Hier werden jedoch quantenmechanische Quasiteilchen als klassische Teilchen, d.h. als gut lokalisiert in Orts- und Impulsraum, behandelt, was sicherlich nicht der Fall ist. Wichtig für die Theorie ist lediglich den Phononen eine Geschwindigkeit und eine Streureate in andere Phononenzustände zuweisen zu können. Das kann vor allem für niedrig dimensionale Systeme zu falschen Ergebnissen führen.

Ein weiterer wichtiger Zugang zu normalem Wärmetransport ist die lineare Antworttheorie. Zunächst wurde diese Theorie von Kubo [81, 82] für die elektrische Leitfähigkeit entwickelt. Darin ist die elektrische Leitfähigkeit einfach proportional zu einer Strom-Strom-Korrelationsfunktion. Diese Korrelationsfunktion wurde im Folgenden ad hoc auf die thermische Leitfähigkeit übertragen durch Ersetzen der elektrischen Ströme durch thermische, was in der berühmten thermischen Kubo-Formel resultierte. Auch die Kubo Formel enthält ein Problem: Während ein elektrisches Potential relativ einfach als Potentialterm in den Hamiltonian eines Quantensystems geschrieben werden kann, ist dies für Temperaturunterschiede sicherlich nicht ohne Weiteres möglich. Damit beruht die Herleitung der Kubo-Formel für den thermischen Fall implizit auf einem Potenzialterm, den es gar nicht gibt. Da dieser Term im Ergebnis, der Strom-Strom-Korrelationsfunktion, nicht mehr auftaucht, machen sich nur die wenigsten Sorgen bei der Anwendung der thermischen Kubo-Formel. Ihre Herleitung jedoch bleibt zunächst zweifelhaft.

In den letzten Jahren ist das Gebiet des Transports von Wärme in Festkörpern wieder mehr ins Zentrum des Interesses gerückt. Wärmeleitung wird sowohl in klassischen als auch in quantenmechanischen Systemen im Zusammenhang mit diversen theoretischen Methoden und Modellen diskutiert. Meist finden jedoch die oben erwähnten Zugänge Verwendung. Trotzdem gibt es einige Experten, die sich nicht sicher sind, ob eine adäquate mikroskopische Erklärung des Wärmetransports überhaupt schon gefunden wurde [8, 14]. Neuere experimentelle Untersuchungen in magnetischen Materialien zeigen erstaunliche Effekte, wie beispielsweise sehr hohe abnormale Leitfähigkeiten [59, 67, 68], was die theoretische Diskussion über die Hintergründe des Wärmetransports weiter anheizt.

Zur Untersuchung von Wärmeleitung gibt es im wesentlichen zwei verschiedene Herangehensweisen: Zunächst kann man, wie es schon Fourier getan hat, ein Quantensystem direkt an Bäder unterschiedlicher Temperatur koppeln. Im stationären *lokalen Gleichgewicht* kann durch die Messung des Temperaturgradienten im System und des Stroms durch das System direkt die Leitfähigkeit entsprechend (E.4) ausgerechnet werden. Eine andere Methode beruht auf der

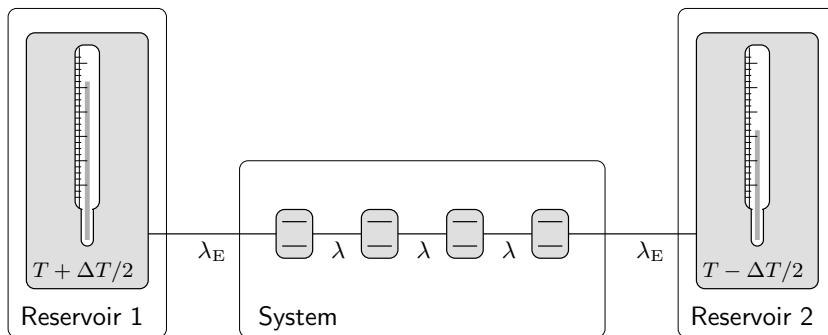


Abbildung E.2.: Kleines Quantensystem gekoppelt an zwei Bäder unterschiedlicher Temperatur.

Beobachtung des Systems beim Zerfall von einer anfänglichen Nichtgleichgewichtsverteilung der Wärme im Material in das globale Gleichgewicht. Als Materialkonstante sollte auch hier die Wärmeleitfähigkeit die zentrale Rolle spielen. Diese beiden Herangehensweisen sind analog zu denen von Einstein und Smoluchowski in ihrer Betrachtung von Diffusion und Brownscher Bewegung [26, 27, 140].

E.2.1. Badkopplung

Koppelt man ein kleines Quantensystem z.B. eine Spinkette an beiden Seiten an Bäder unterschiedlicher Temperatur (siehe Abb. E.2) nach der Methode der Quantenmastergleichung, findet man abhängig von der internen Kopplung des Systems unterschiedliches Transportverhalten. So zeigt ein System mit ausschließlich energieaustauschender Kopplung ballistisches Transportverhalten, während eine Heisenbergkette bzw. ein zufällig gekoppeltes System normalen diffusiven Transport zeigt. Dies bedeutet man findet bei letzter genannten Systemen tatsächlich ein reguläres thermodynamisches Verhalten, d.h. das Gesetz von Fourier ist erfüllt.

Mittels einer Störungstheorie im Liouvilleraum kann nun das entsprechende Verhalten analytisch bestätigt werden. An Stelle der bekannten Störungstheorie im Hilbertraum wird hier im höherdimensionalen Liouvilleraum gearbeitet, in dem auch die oben erwähnten Dissipatoren als Superoperatoren definiert sind. Die ungestörte Situation ist definiert als das System gekoppelt an zwei Bäder gleicher Temperatur, während das Anschalten des äußeren Temperaturgradienten als Störung betrachtet wird. Eine analog zum Hilbertraum durchgeführte Störungstheorie führt nun zur Kubo-Formel im Liouvilleraum,

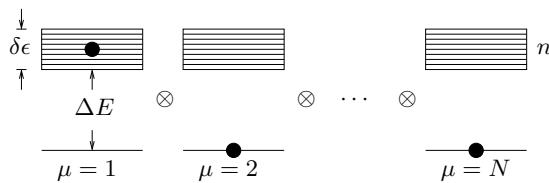


Abbildung E.3.: Quantenthermodynamisches Modellsystem zur Untersuchung von Wärmeleitung.

mit deren Hilfe Wärmeströme und Temperaturgradienten in den angesprochenen konkreten Modellsystem berechnet werden können. Durch die Herleitung im Raum der Dissipatoren (Liouvilleraum) enthält diese Theorie keine fragwürdigen Potentiale mehr im Unterschied zur Standard-Kubo-Formel.

Aus Strömen und Temperaturunterschieden kann auch hier die Wärmeleitfähigkeit bestimmt werden, die nicht vom äußeren Temperaturunterschied der Bäder abhängt. Leider hängt die Leitfähigkeit jedoch noch in nichttrivialer Weise von der Kopplungsstärke der Bäder ab. Es steht zu hoffen, dass in zukünftigen Untersuchungen in längeren Ketten diese Abhängigkeit verschwindet, da eine Materialeigenschaft nur von den Parametern des Systems abhängen sollte.

E.2.2. Hilbertraummittelmethode

Zur Betrachtung der Wärmeleitung ist es zunächst notwendig ein System mit topologischer Struktur im Ortsraum zu verwenden. Das entsprechende Modellsystem ist in Abb. E.3 gezeigt und besteht aus kleinen endlichdimensionalen Untereinheiten, jeweils mit einem Grundzustand und einem Band gleichverteilter Niveaus einheitlicher Breite. Gekoppelt sind diese Untereinheiten durch eine schwache energieaustauschende Kopplung. Offensichtlich eignet sich die Hilbertraummittelmethode ausgezeichnet diese Modellsysteme zu behandeln. Vor allem die Möglichkeit endliche Systeme innerhalb einer solchen Betrachtung zu untersuchen ist an das gegebene Modellsystem hervorragend angepasst.

Hier werden nun nicht wie oben besprochen Bäder unterschiedlicher Temperatur angekoppelt, sondern der Zerfall des Systems in den globalen Gleichgewichtszustand beobachtet. Der Anfangszustand ist durch die schwarzen Punkte in Abb. E.3 angedeutet: wir starten mit einer Anregung im ersten System und erwarten den Zerfall in einen Zustand mit gleichverteilter Energie. Genau wie in Abschnitt E.1.2 kann hier wieder die Zeitentwicklung des Zustand des Gesamtsystems als Kurzzeitnäherung in Dyson-Entwicklung betrachtet wer-

den. Die interessante Größe ist nun die Wahrscheinlichkeit P_μ das System irgendwo im angeregten Band anzutreffen, gegeben durch den Projektator \hat{P}_μ auf den entsprechenden Subraum. Dies bedeutet, dass wir das System in einer vergrößerten Weise betrachten, uns also nicht für den exakten mikroskopischen Zustand interessieren. Nach der Mittelung über die entsprechenden Zustände im Gesamthilbertraum erhält man eine Ratengleichung für die Wahrscheinlichkeiten

$$\frac{dP_1}{dt} = -\kappa(P_1 - P_2) , \quad (\text{E.5})$$

$$\frac{dP_\mu}{dt} = -\kappa(2P_\mu - P_{\mu+1} - P_{\mu-1}) , \quad \mu = 2, \dots, N-1 , \quad (\text{E.6})$$

$$\frac{dP_N}{dt} = -\kappa(P_N - P_{N-1}) \quad (\text{E.7})$$

mit der Energiediffusionskonstante κ , die nur von der Kopplungsstärke der Untereinheiten und der Zustandsdichte im Band, also nur von Systemparametern, abhängt. In diesem einfachen Modellsystem ist die Energie U_μ in einer Untereinheit gegeben durch die Wahrscheinlichkeit P_μ multipliziert mit der Energielücke ΔE . Damit kann aber auch der Energiestrom zwischen zwei Untereinheiten ausgerechnet werden und man erhält nach einiger Rechnung das „Fourier Gesetz der Energie“

$$J(\mu + 1, \mu) = -\kappa(U_{\mu+1} - U_\mu) . \quad (\text{E.8})$$

Das ursprüngliche Gesetz von Fourier kann in der obigen Situation nicht direkt untersucht werden, da es sicherlich nur für kleine Unterschiede in der Temperatur definiert ist, was für den oben gewählten Anfangszustand nicht gilt. Deshalb wird nun ein Zustand mit einem definierten, kleinen Temperaturgradienten im System als Anfangszustand gewählt. So kann tatsächlich auch der thermische Fall in obigem Modell untersucht werden und man findet das *Fourier Gesetz*

$$J_{\text{th}}(\mu + 1, \mu) = -\kappa_{\text{th}} \Delta T(\mu + 1, \mu) , \quad (\text{E.9})$$

wobei sich die thermische Leitfähigkeit als Produkt obiger Energiediffusionskonstante und der spezifischen Wärme einer Untereinheit ergibt. Die theoretischen Rechnungen werden durch numerische Simulation hervorragend bestätigt. Damit ist es nun wirklich gelungen auch den Wärmetransport und die damit verbundenen Größen direkt auf die Quantenmechanik aufzubauen.

E.3. Fazit

Zusammenfassend kann man sagen, dass es in der vorliegenden Arbeit gelungen ist Relaxation ins Gleichgewicht sowie Diffusion von Wärme in kleinen Quantensystemen mittels der neuen Hilbertraummittelmethode sowie die Theorie offener Quantensysteme zu untersuchen. Das genauere Verständnis dieser beiden wichtigen Prozesse ist von zentraler Bedeutung nicht nur für die Fundierung der Thermodynamik auf Basis einer mikroskopischen Theorie sondern auch für die Technische Bewältigung der Probleme einer Fortschreitenden Miniaturisierung. Die Grenzen der Anwendbarkeit der klassischen Thermodynamik in nanoskopischen Systemen, beispielsweise in Computerchips, können schon bald erreicht sein. Trotzdem zeigt die vorliegende Untersuchung, dass auch in sehr kleinen Systemen thermodynamische Eigenschaften durchaus noch Bestand haben können. Darüberhinaus sind vor allem neue Eigenschaften, die über die klassische Thermodynamik hinaus gehen, interessant. Könnte es beispielsweise so etwas wie Wärmesupraleitung geben, nachdem einige magnetische Materialien eine sehr hohe abnormale (magnetische) Wärmeleitfähigkeit besitzen.

Somit ist neben der Fundierung von Nichtgleichgewichtsphänomenen auf Basis der Quantenmechanik (also die Nichtgleichgewichtsquantenthermodynamik) auch die Erweiterung der Konzepte der Thermodynamik auf nanoskopische Skalen nahe am Gleichgewicht von entscheidender Bedeutung. Es steht zu hoffen, dass die vorliegende Arbeit zur Verbindung von Quantenmechanik und Thermodynamik auch im Nichtgleichgewichtsbereich und auf nanoskopischer Ebene beitragen kann.

List of Symbols

BA	Born Approximation
HAM	Hilbert Space Average Method
QME	Quantum Master Equation
RWA	Rotating Wave Approximation
$\llbracket \dots \rrbracket$	Hilbert space average
$\Delta_H = \llbracket \alpha^2 \rrbracket - \llbracket \alpha \rrbracket^2$	Hilbert space variance
$[\dots, \dots], [\dots, \dots]_+$	Commutator, anticommutator
$ \dots\rangle, \langle \dots $	State, adjoint state in Liouville space (vector notation)
$(\dots \dots)$	Scalar product in Liouville space
∇	Nabla operator
$\hat{1}_{S/E}$	Unit operator in the respective subspace S, E
$\hat{\alpha}$	Hilbert space average under side conditions
\hat{A}_α	System operator in the interaction Hamiltonian
$\mathfrak{a}, \mathfrak{b}$	Smallness parameters in perturbation theory
$\hat{\mathfrak{A}}, \hat{\mathfrak{G}}, \dots$	Super operators in Liouville space
$\{ A_j\rangle\}, \{ A^j\rangle\}$	Basis, dual basis in Liouville space
β, β_E	Inverse temperature, inverse environmental temperature
\hat{b}_k	Bosonic annihilation operator
\hat{B}_α	Environmental operator in the interaction Hamiltonian
k_B	Boltzmann constant
\hat{c}_k	Fermionic annihilation operator
$\hat{C}_{ij,ab}$	Subpart of the interaction operator
\hat{C}_{ij}	Environmental part of the interaction
$c, c(T)$	Heat capacity
C_F	Förster coupling constant
C_{NR}	Nonresonant coupling constant
δ_{ij}	Kronecker delta
\hat{D}	Dyson short time evolution operator
d	Dimension of the Liouville space
D^2	Time averaged quadratic deviation of HAM
ΔE	Level splitting in the system, gap energy

$\delta\epsilon$	Band width
$\hat{\mathfrak{E}}$	Time independent perturbation operator
$\hat{\mathfrak{E}}_i^{\downarrow/\uparrow}$	Transition super operator
E	Internal energy, energy of the complete system
$E(\mu)$	Internal energy of μ th subunit
E_a	Mean band energy of a th band
E_n	Eigenenergies of the system Hamiltonian
$f(t)$	Switch on function
$f_{ij,ab}(\tau)$	Integrated environmental correlation function
$g(\tau)$	Correlation function, integrand of $f_{ij,ab}(\tau)$
$\gamma_{\alpha\beta}(\omega), \gamma_\alpha$	Transition rates
$\gamma_{ij,ab}$	Rate (like in Fermi's Golden Rule)
$\Delta\hat{H}_{\text{loc}}(\mu, \mu + 1)$	Operator of energy difference of adjacent sites
\hat{H}'_t	Perturbation potential (explicitly time dependent)
$\mathcal{H}, \mathcal{H}_E, \mathcal{H}_S$	Hilbert space (for environment E, system S)
\hat{H}	Hamiltonian
\hat{H}_{int}	Interaction part of the Hamiltonian
\hat{H}_{loc}	Local part of the Hamiltonian
\hat{H}_{SE}	System environment interaction Hamiltonian
\hat{H}_F	Förster interaction Hamiltonian
\hat{H}_H	Heisenberg interaction Hamiltonian
\hat{H}_{NR}	Non-resonant interaction Hamiltonian
\hat{H}_R	Random interaction Hamiltonian
\hat{H}_S, \hat{H}_E	Local Hamiltonian of the system S/environment E
$\hat{J}(\mu, \mu + 1)$	Energy (heat) current operator between μ and $\mu + 1$
\mathbf{J}	Heat, energy current
$J, J(\mu, \mu + 1)$	Current expectation value
κ	Heat (energy) conductivity, diffusion constant
κ'	Global conductivity
$\kappa(\mu, \mu + 1)$	Local conductivity
$\kappa(E, \mathcal{E}, \mathcal{E}')$	General heat conductivity
κ_{th}	Thermal conductivity
$\hat{\mathfrak{K}}$	Memory kernel, super operator
λ, λ_0	Coupling strength
λ_{can}	Canonical coupling strength
λ_E	External coupling strength
λ_{mic}	Microcanonical coupling strength
$\lambda_{ij,ab}$	Interaction strength of $\hat{C}_{ij,ab}$
\mathcal{L}	Liouville space
$\hat{\mathfrak{L}}$	Liouvillian, Liouville super operator

$\hat{\mathcal{L}}(\Delta T, t)$	Reservoir perturbation operator
$\hat{\mathcal{L}}(t)$	Liouvillian in interaction picture
$\hat{\mathcal{L}}_0$	Unperturbed Liouvillian
$\hat{\mathcal{L}}_i$	i -th reservoir dissipator
$\hat{\mathcal{L}}_E$	Dissipator, super operator
$\hat{\mathcal{L}}_S$	Coherent Liouvillian, super operator
\hat{L}_α	Lindblad environmental operator
l_j	Eigenvalues of $\hat{\mathcal{L}}_0$
μ	Index of a subunit
$ n_a\rangle$	Eigenstate in the a th band (e.g. $a = A, B$)
$ n\rangle$	Eigenstate of the system Hamiltonian
N	Number of subunit
n	State in a subunit, Hilbert space dimension
$n(E, \mathcal{E})$	Number of levels in the band (E, \mathcal{E})
N_a	Number of levels in the a th band (e.g. $a = A, B$)
$\omega_{ij}, \omega_{n_A, n_B}$	Transition frequency in the system/environment
ω_{uv}	Displaced transition frequency in the environment
$\hat{\Pi}_a$	Projection operator to the a th band
$\hat{P}_{\mu, \nu}$	Transition, projection operator, heat conduction model
$\hat{P}_{ij, a}$	Special projection/transition operator
\hat{P}_{ij}	Projection/transition operator in the system
$\hat{\mathfrak{P}}$	Super operator, projector to the relevant part
ϕ_i	State amplitudes
$P(E, \mathcal{E})$	Probability distribution in the complete system
P_i	Probability of state i
P_μ	Probability of an excitation in the μ th subunit
$P_{ij, a}$	Expectation value of $\hat{P}_{ij, a}$
P_{ij}	Conditional probability for state i and j
$ \psi_\mu\rangle$	Part of the state according to subunit μ
$\hat{\mathfrak{Q}}$	Super operator, projector to the irrelevant part
$\hat{\rho}$	Density operator
$\hat{\rho}(\mu)$	Reduced density operator of μ th subsystem
$ \Delta\hat{\rho}(t)\rangle$	Nonequilibrium part of the stationary state
$ \hat{\rho}_0\rangle$	Stationary state of $\hat{\mathcal{L}}_0$
$ \hat{\rho}_j\rangle$	Eigenvectors of $\hat{\mathcal{L}}_0$
$ \hat{\rho}_{\text{leq}}\rangle$	Local equilibrium state
ρ_{ij}	Matrix components of the density operator
$\hat{\rho}_{\text{eq}}$	Canonical equilibrium state
$\hat{\rho}_S, \hat{\rho}_E$	Density operator of the system S/environment E
$\hat{\rho}_{\text{SE}}$	System environment density operator

$\hat{S} = \hat{D}^\dagger \hat{P}_{ij,a} \hat{D}$	Short time evolution of $\hat{P}_{ij,a}$
$\hat{\sigma}_+, \hat{\sigma}_-$	Raising, lowering operators
$\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$	Pauli operators
$\sigma_{ij}(\omega)$	Electrical response coefficient
S	Von-Neumann entropy
$S_{0/1/2}$	Orders of the time evolution equation
ΔT	Temperature difference
$\delta T(\mu, \mu + 1)$	Local temperature difference
τ	Short time step
$\tau_{1/2}$	Starting/Ending time of linear regime
T	Temperature, mean temperature
$T(\mathbf{r}, t)$	Temperature field
T_{dec}	Decoherence time
T_E	Reservoir Temperature
T_{th}	Thermalization time
$T_{\text{u/l}}$	Thermalization time upper/lower subspace
τ_c	Decay time of correlation function
τ_D	Break down time of Dyson series expansion
\hat{U}	Time evolution operator
$\hat{U}_{\text{diag/off}}$	Diagonal/off-diagonal part of \hat{U}_2 (2nd order)
$u(T(\mathbf{r}, t))$	Energy density
U_μ	internal energy of μ th subunit
\hat{V}	Interaction operator
\hat{V}_{can}	Canonical part of the interaction
\hat{V}_{mic}	Microcanonical part of the interaction
$\hat{\mathfrak{V}}$	Basis transformation super operator
$\Delta\omega$	Frequency distance of adjacent levels
ω_k	Dispersion relation
$W_i^{\downarrow/\uparrow}$	Transition rate
$W_{ij}(T, \lambda_E)$	Rates $i \rightarrow j$
\mathbf{X}_j	Generalized external force
$\xi = \lambda_{\text{mic}}/\lambda_{\text{can}}$	Relative microcanonical coupling strength
Z_{ij}	Response coefficient
Z	Canonical partition function

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- [i] J. Gemmer, R. Steinigeweg, and M. Michel. Validity of the Kubo formula for thermal conduction. *Phys. Rev. B*, **73**, 104302, (2006).
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