

1. Introduction

Quantum-statistical mechanics is a very rich and checkered field. It is the theory dealing with the dynamical behavior of spontaneous quantal fluctuations.

When probing dynamical processes in complex many-body systems, one usually employs an external force which drives the system slightly or far away from equilibrium, and then measures the time-dependent response to this force. The standard experimental methods are quasielastic and inelastic scattering of light, electrons, or neutrons off a sample, and the system's dynamics is analyzed from the line shapes of the corresponding spectra. Other experimental tools are, e. g., spin relaxation experiments, studies of the absorptive and dispersive acoustic behavior, and investigations of transport properties. In such experiments, the system's response gives information about the dynamical behavior of the spontaneous fluctuations. Theoretically, the response is rigorously described in terms of time correlation functions. Therefore, time correlation functions are the center of interest in theoretical studies of the relaxation of non-equilibrium systems.

This book deals with the theories of open quantum systems with emphasis on phenomena in condensed matter. An essential ingredient of any particular real dissipative quantum system is the separation of a global quantum system into a subsystem, usually called the relevant part, and the environment, called the irrelevant part. In most cases of practical interest, the environment is thought to be in thermal equilibrium. The coupling to a quantum statistical environment results in a fluctuating force acting on the relevant system and reflecting the characteristics of the heat reservoir. It is the very nature of the fluctuating forces to cause decoherence and damping, and to drive everything to disorder.

While quantum mechanics was conceived as a theory for the microcosm, there is apparently no contradiction with this theory in the mesoscopic and macroscopic world. The understanding of the appearance of classical behavior within quantum mechanics is of fundamental importance. This issue is intimately connected with the understanding of decoherence. Despite the stunning success of quantum theory, there is still no general agreement on the interpretation. The main disputes circle around "measurement" and "observation".

Decoherence is the phenomenon that the superposition of macroscopically distinct states decays on a short time scale. It is omnipresent because information about quantum interference is carried away in some physical form into the surroundings. In a sense, the environmental coupling acts as a continuous measuring apparatus, leading to an incessant destruction of phase correlations. The relevance of this coupling for macroscopic systems is nowadays generally accepted by the respectable community.

This is a book of methods, techniques, and applications. The level is such that anyone with a first course in quantum mechanics and rudimentary knowledge of path integration should not find difficulties. An attempt is made to present the problem of dissipation in quantum mechanics in a unified form. A general framework is devel-

oped which can deal with weak and strong dissipation, and with all kinds of memory effects. The reader will find a presentation of the relevant ideas and theoretical concepts, and a discussion of a wide collection of microscopic models. In the models and applications, emphasis is put on condensed matter physics. We have tried to use vocabulary and notation which should be fairly familiar to scientists working in chemical and condensed matter physics.

The book is divided into five parts. The following sequence of topics is adopted. The first part of the book is devoted to the general theory of open quantum systems. In Chapter 2, we review traditional approaches, such as formulations by master equations for weak coupling, operator-valued and quasiclassical Langevin equations. We also discuss attempts to interpret the dynamics of an open quantum system in terms of a stochastic process in the Hilbert space of state vectors pertaining to the reduced system. In Chapter 3, various global models are introduced. They are partly connected with microscopic models which are of relevance in condensed matter physics. Chapter 4 is devoted to the equilibrium statistical mechanics for the relevant subsystems of these models using the imaginary-time path integral approach. Chapter 5 concerns dynamics — quantum-mechanical motion, decoherence and relaxation of macroscopic systems that are far from or close to equilibrium. In particular, we discuss the concepts of preparation functions, propagating functions, and correlation functions and derive the corresponding exact formal solutions using the path integration method.

Part II with Chapters 6 – 9 covers a discussion of exactly solvable damped linear quantum systems (damped harmonic oscillator and free Brownian particle), the useful thermodynamic variational approach with extension to open nonlinear quantum systems, and a semiclassical treatment of the quantum decoherence problem for a particle traveling in a medium.

Part III deals with quantum-statistical metastability: a problem of fundamental importance in chemical physics and reaction theory. After an introduction into the problem in Chapter 10, the relevant theoretical concepts and the characteristic features of the decay are discussed in Chapters 11 to 17. The treatment mainly relies on a thermodynamic method in which the decay rate is related to the imaginary part of the analytically continued free energy of the damped system. This allows for a uniform theoretical description in the entire temperature range. The discussion extends from high temperatures where thermal activation prevails down to zero temperature where the system can only decay by quantum-mechanical tunneling out of the ground state in the metastable well. Results in analytic form are presented where available.

In Part IV, we consider the thermodynamics and dynamics of the dissipative two-state or spin-boson system. This is the simplest nonlinear system for the study of the interplay between quantum coherence, quantal and thermal fluctuations, and friction. After an introduction into the model in Chapter 18, the discussion in Chapter 19 is focused on equilibrium properties for a general form of the system-reservoir coupling. In particular, the partition function is discussed and the specific heat and static susceptibility are studied. The relationship with Kondo and Ising models is explained.

Chapter 20 is devoted to the electron transfer problem in a solvent, nonadiabatic tunneling under exchange of energy, and single charge tunneling in the presence of an electromagnetic environment. Chapter 21 deals with the dissipative two-state dynamics. Different kinds of initial preparations of the system-plus-reservoir complex are treated and exact formal expressions for the system's dynamics in the form of series expressions and generalized master equations are derived. Ample space is devoted to the discussion of non-equilibrium and equilibrium correlation functions, and to adequate approximate treatments in the various regions of the parameter space. Part IV closes with a chapter on the dynamics of the dissipative two-state system under exposure to time-dependent external fields.

The last part reviews dissipative quantum transport of a quantum Brownian particle in a tilted cosine potential. In Chapters 23 and 24, we introduce the respective global models in the weak- and strong-tunneling representations. We present the appropriate nonequilibrium quantum transport formalism and derive exact formal expressions describing the system's dynamics for factorizing and thermal initial states. Furthermore, explicit solutions in analytic form in various limits are given. Chapter 25 provides a discussion of a duality symmetry between the weak- and strong-tunneling representations which becomes an exact self-duality in the so-called Ohmic scaling limit. We show that self-duality offers the possibility to construct the exact scaling function for the nonlinear mobility at zero temperature. In addition, the full counting statistics of these generic quantum transport models is discussed. The book closes with a chapter on quantum transport of charge in quantum impurity models. Both the weak- and strong-tunneling representations are discussed. In addition, the close relationship of the quantum impurity model with the Brownian particle model, and with charge transport in a coherent conductor and in Josephson systems is pointed out. This allows us to translate results obtained for one of these system in corresponding results for related other systems.

We have tried to concentrate on models which are simple enough to be largely tractable by means of analytical methods. There are, however, important examples where numerical computations have given clues to the analytical solution of a problem. If one wishes to calculate the full dynamics of the global system, one is faced with the problem that the number of basis states is growing exponentially. Therefore, even on supercomputers, the number of reservoir modes which can be treated numerically exactly, is rather limited. When the number of bath modes is above ten or even tends to infinity, an inclusive description of the environmental effects, e.g., in terms of the influence functional method (cf. Chapters 4 and 5) is indispensable. Various numerical schemes developed within the framework of the influence functional approach are available. The most valuable numerical tool in many-body quantum theory is probably the path integral Monte Carlo simulation method. Unfortunately, in simulations of the real-time quantum dynamics, the numerical stability of long-time propagation is spoilt by the destructive interference of different paths contributing to the path sum. This so-called *dynamical sign problem* is intrinsic in real-time quantum

mechanics, and is characterized by an exponential drop of the signal-to-noise ratio with increasing propagation time.

In recent years, considerable progress in reducing the sign problem has been achieved by implementation of blocking algorithms in quantum Monte Carlo simulations based on a Trotter split-up of the elementary propagator. A possible strategy consists in sampling “blocks” of which the corresponding average sign is nonzero, instead of single states. This method always reduces the sign problem [C. H. Mak and R. Egger, *Adv. Chem. Phys.* **93**, 39 (1996)]. Alternatively, one may use iterative procedures which are based on systematic approximations. In the so-called tensor-propagator approach, a maximal correlation time of the influence functional interactions is introduced [N. Makri, *J. Math. Phys.* **36**, 2430 (1995)]. In the so-called path class approach, the exact summation of a class of paths is approximated by a low-order cumulant expansion of averages of the path class history [M. Winterstetter and W. Domcke, *Chem. Phys. Letters* **236**, 455 (1995)]. As an alternative method, Stockburger and Grabert proposed to unravel the Feynman-Vernon influence functional into a stochastic one, and to solve numerically the ensuing stochastic Liouville-von Neumann equations, or the related stochastic Schrödinger equations, which are free of quantum memory effects [J.T. Stockburger and H. Grabert, *Phys. Rev. Lett.* **88**, 170407 (2002)]. We have refrained from adding sections which deal with numerical methods in detail. Where appropriate, we give relevant information and literature.

After all, the reader may not find a comprehensive account of what interests him most. Since the number of articles in this general field has become enormous in recent years, a somewhat arbitrary choice among the various efforts is inevitable. My choice of topics is just one possibility. It reflects, to some extent, the author’s personal valuation of an active and rapidly developing area in science.