Quantum dynamics in strong fluctuating fields

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A large number of multifaceted quantum transport processes in molecular systems and physical nanosystems, such as e.g. nonadiabatic electron transfer in proteins, can be treated in terms of quantum relaxation processes which couple to one or several fluctuating environments. A thermal equilibrium environment can conveniently be modelled by a thermal bath of harmonic oscillators. An archetype situation provides a two-state dissipative quantum dynamics, commonly known under the label of a spin-boson dynamics. An interesting and nontrivial physical situation emerges, however, when the quantum dynamics evolves far away from thermal equilibrium. This occurs, for example, when a charge transferring medium possesses nonequilibrium degrees of freedom, or when a strong time-dependent control field is applied externally. Accordingly, certain parameters of underlying quantum subsystem acquire stochastic character. This may occur, for example, for the tunnelling coupling between the donor and acceptor states of the transferring electron, or for the corresponding energy difference between electronic states which assume via the coupling to the fluctuating environment an explicit stochastic or deterministic time-dependence. Here, we review the general theoretical framework which is based on the method of projector operators, yielding the quantum master equations for systems that are exposed to strong external fields. This allows one to investigate on a common basis, the influence of nonequilibrium fluctuations and periodic electrical fields on those already mentioned dynamics and related quantum transport processes. Most importantly, such strong fluctuating fields induce a whole variety of nonlinear and nonequilibrium phenomena. A characteristic feature of such dynamics is the absence of thermal (quantum) detailed balance.

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1. Introduction

The description and analysis of the dynamics of open quantum systems, i.e., quantum systems interacting with a dissipative environment, presents a key challenge for non-equilibrium statistical physics. Moreover, this theme is also of prominent importance for many applications in physics, physical chemistry and physical biology. This can be exemplified by the relaxation dynamics occurring in a two-level quantum system that is coupled to the vibrational degrees of freedom of an environment. This latter theme gained great popularity and is known under the label of "spin-boson dynamics" [1–4]. Several apparently different physical problems can formally be unified within such a common mathematical description. For example, the relaxation dynamics of a nuclear spin 1/2 in solids, the tunnelling of defects in metals, the relaxation dynamics of atoms in optical cavities can all be modelled by (pseudo)-spin-boson dynamics. Another important and relevant situation refers to donor–acceptor electron transfer (ET) reactions in various molecular structures [5–9]. For spatially extended quasi-periodic molecular structures like those formed by protein α-helices [10–13], or DNA's [14–18] many quantum states are generally required to describe charge

transfer processes. Here, a multi-state tunnelling problem naturally emerges with the tight-binding model serving as one of the simplest theoretical frameworks.

The primary problem is to describe the influence of the environmental degrees of freedom on the quantum dynamics of interest. Many different approaches have been developed to tackle this challenge. The fundamental methodology consists in separating the total system into two (or more) mutually interacting parts: the dynamical subsystem with a small number of relevant degrees of freedom and a thermal bath represented by a huge number of microscopic degrees of freedom which are at thermal equilibrium. A most general quantum-mechanical description is provided by the density operator of the whole, combined system which depends both on the variables of the considered dynamical subsystem (relevant variables) and the variables of the thermal bath (irrelevant variables). The dynamical behaviour of a small quantum subsystem presents the focus of interest with the thermally equilibrated bath degrees of freedom serving as a source of randomness for the relevant dynamics. This randomness can effectively be eliminated via a course-grained description of the system of interest. A corresponding averaging procedure results in a contracted, reduced dynamics which generally entails memory effects, decoherence and dissipation.

Different approaches have been developed over the years within this general line of reasoning. Within a variety of different approaches, the method of path-integrals in real time [1, 2, 19–21] and the projection operator method [22–31] provide some of the most frequently used methods. The path-integral approach can, however, be technically cumbersome in practical applications of interest. The projection operator method appeals because of its generality and technical elegance. It allows one to obtain formally exact generalised master equations (GMEs) for the reduced density matrix in a straightforward way. By and large, however, such exact GMEs cannot be analytically elaborated further without invoking some sort of a perturbation technique with corresponding approximations. For example, already the seemingly simple spin-boson dynamics cannot be solved analytically exactly. The weak-coupling approximation of the system-bath coupling is one of the most useful and commonly employed schemes. Moreover, a strong-coupling problem can often be mapped onto a (different) weak-coupling problem within a canonically transformed basis of the *total* system. The projection operator method, combined with appropriate canonical transformations, further improved by use of variational approaches, presents a powerful and general method of wide acceptance. This well-established methodology is, however, also rather demanding.

Yet another popular methodology consists in modelling the thermal bath influence through a classical stochastic field which acts upon the considered dynamical system. Formally, this methodology corresponds to introduction of randomly fluctuating time-dependent forces in the Hamiltonian of considered quantum system [32–35] and, finding subsequently the stochastically averaged evolution of the considered system which is governed by a stochastic Liouville–von Neumann equation. This methodology is known under the label of stochastic Liouville equation (SLE) approach [34–41]. Due to a reasoning that involves the central limit theorem, classical random forces with Gaussian statistics are most frequently used in this kind of approximate modelling. The Gaussian white noise serves here as the simplest implementation for the corresponding classical stochastic bath. It corresponds to a bath

with an infinite spectrum of excitations. Such models can be solved exactly in a number of specific cases [35, 38, 40–44]. All the thermal baths possess, however, finite energy spectra. This circumstance gives rise to temporal autocorrelations in the bath-induced classical stochastic fields. Gaussian-Markov noise with the exponentially decaying temporal autocorrelations presents one of the simplest models of such more realistic, coloured noise [45]. Yet, even in the simplest case of a two-state tunnelling system this model cannot be solved exactly except for some limiting cases (see, e.g., in [46] for the Landau-Zener model with a stochastic modulation). Generically one must invoke some approximations; e.g., in the case of a weakly coloured Gaussian noise some kind of cumulant expansion technique [38, 39, 47] can be used.

There exists a different possibility. Continuous state noises can be approximated by noise sources with a large number of discrete states (e.g., by a discretisation procedure of a continuous diffusion process in a potential). Certain Markovian discrete state noises provide then a rather general framework for a formally exact stochastic averaging [34, 48, 49]. Moreover, the two-state Markovian noise (also known as *dichotomous noise*) presents such a simple discrete noise source which allows for an exact study of noise-driven two-level quantum systems [45, 50–56]. In addition, the multistate case of exciton transfer in molecular aggregates with many quasi-independent noise sources modelled by independent two-state Markovian noises presents another analytically tractable case, in the sense that it can be reduced to the solution of a system of linear differential equations with constant coefficients for averaged dynamics [57]. The discussed dichotomous noise can model a quasi-spin 1/2 stochastic bath variable. In the case of ET in molecular systems such a quasi-spin stochastic variable can simulate, for example, the bistable fluctuations of a charged molecular group nearby the donor, or acceptor site, or the conformational fluctuations of a bistable molecular bridge.

A well-known drawback of the SLE approach consists, however, in the asymptotic equal-population of the energy levels of quantum system which occurs for arbitrary energy differences [38, 40, 41]. This means that the SLE approach corresponds formally to an infinite bath temperature. At least, the thermal energy $k_B T$ should thus be larger than the characteristic energy scale of the quantum system, e.g., larger than the energy width of the corresponding excitonic band. This corresponds to a high-temperature approximation [40, 41, 52, 57]. The reason for this intrinsic restriction is that the stochastic field unidirectionally drives the quantum system without being modified by the system's feedback (no back reaction). This drawback within the SLE approach requires some *ad hoc* corrections to enforce the correct thermal equilibrium [42, 58, 61]. Nevertheless, the SLE approach can yield a very useful tool, notably in the nuclear magnetic resonance (NMR) theory [40, 59], the theory of exciton transfer in molecular aggregates [40] and within the theory of single-molecular spectroscopy [60].

Combined scenarios have been used in several works [61–63]. Initially, those were aimed to model the influence of relaxation processes in the thermal bath [61], or to account for non-Gaussian large-amplitude fluctuations of molecular charged groups [62]. However, it was soon recognised that the addition of classical noise to a dissipative quantum dynamics generally violates the detailed balance symmetry at the environmental temperature [64]. Therefore, the stochastic field in these approaches

correspond physically to a nonequilibrium noise influence. It has been shown theoretically that such a nonequilibrium non-Gaussian (e.g., two-state) noise can regulate the quantum transition rates by several orders of magnitude [62, 64–66]. Moreover, it may pump energy into the quantum system. This in turn gives rise to various interesting nonlinear nonequilibrium phenomena such as a noise-induced enhancement of thermally assisted quantum tunnelling [67], an inversion of population in discrete quantum dissipative systems [68], a noise-induced absolute negative mobility (ANM) for quantum transport [69], or also a fluctuation-induced transport of quantum particles within a tight-binding description [70], to name the most prominent ones. From a thermodynamical perspective these nonequilibrium effects are due to a virtual presence of two heat baths of different nature: a first one assuming the temperature of the environment T (modelled by a thermal bath of harmonic oscillators that are bi-linearly coupled to the relevant system), another one possessing a virtually infinite temperature $T_\sigma = \infty$ (stochastic bath). In this intuitive picture, a nonequilibrium stochastic field is expected to heat the quantum-mechanical degrees of freedom, causing various, surprising nonequilibrium phenomena.

The study of the dynamics of such quantum dissipative systems which are driven far from thermal equilibrium by nonequilibrium fluctuations is the focus of present work. The situation here is similar in spirit to one in the recently emerged field of (classical) Brownian motors [71–76], see, e.g., in [77–81] for surveys and further references.

In this review, we present a general outline with many important examples given of the following methodology: The nonequilibrium stochastic field is represented by an external time-varying classical field in the Hamiltonian of the quantum system. This field is treated without invoking any further approximation, until it becomes necessary to do so. In doing so, a formally exact GME is obtained which includes the external field both in the dynamical part and in the dissipative kernel of the GME exactly. Subsequently, the dissipative kernel is expanded to the lowest order, i.e. the second order in the system-bath coupling. [In a properly canonically transformed basis this scheme allows one to study the opposite limit of strong dissipation/weak tunnelling as well.] The overall procedure results in an approximate, GME for the reduced density matrix of the considered, relevant quantum system. We recall that within this methodology the external field is not only included exactly in the dynamical part, but it modifies as well the dissipative kernel in a very profound manner. In particular, the dissipative kernel becomes a retarded functional of the driving field. Thereby, the field influence on quantum dynamics is taken rigorously into account within the given order of the system-bath coupling. Such a corresponding modification of the dissipative kernel becomes crucial for strong driving fields.

This so-tailored approach allows one to describe stochastic and time-periodic fields on equal grounds. The influence of a time-periodic driving on the dissipative quantum dynamics has been investigated in [68, 82, 83, 85–87]. Other related work has been done at the same time and in parallel by several other research groups elaborating similar [88–90], or different [84, 91–97] approaches which reconcile within some approximations [3, 4, 87, 98, 99].

The difference between the stochastic fields and the periodic fields enters within our approach on the level of averaging of the corresponding field-driven GMEs.

In this context, one must refer to some further approximations, which generally are based on the separation of time-scales involving the external driving, the contracted quantum dynamics and the decay of dissipative kernels in the GMEs. Remarkably, in the case of dichotomous fluctuations this averaging can be done exactly without further approximations [67, 100, 101]. The spin-boson model driven by such dichotomous Markovian fluctuations presents one instance of general interest which has been studied in detail in [67, 68, 85, 86, 101]. Two other important situations, where an exact averaging is feasible for a broad class of stochastic and periodic processes, are given by an infinitely extended tight-binding model. These are: (i) the case of coherent tunnelling in the absence of dissipation and (ii) the regime of incoherent tunnelling (strong dissipation) when the tunnelling is weak (high tunnelling barriers). Some explicit pertinent examples are discussed in [70, 102–104].

This review is organised as follows, see in figure 1. The study of a quantum dynamics subjected to non-Markovian stochastic fields that are modelled by discrete state processes of the renewal type is presented in section 2. Therein, a formally exact averaging of the quantum evolution over the stationary realisations of stochastic fields is given. The general results are illustrated by a new Laplace-transformed exact solution of averaged two-level quantum dynamics driven by a symmetric non-Markovian two-state field. The prior results for a quantum two-level dynamics driven by a dichotomous Markovian field are reproduced as a particular limiting case. This section contains the results for the fluctuating Kubo oscillator and also a short primer into the projection operator formalism. Two-state quantum dynamics in strong-periodic fields is considered in section 3. Section 4 outlines

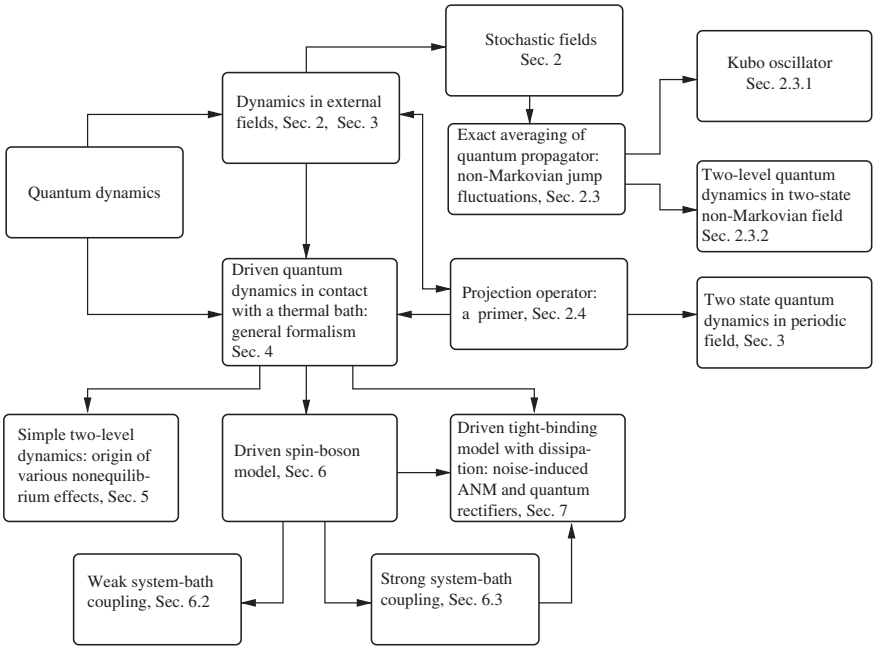

Figure 1. A flow diagram depicting the various topics and their mutual interrelations which are covered by this review.

the general formalism of dissipative quantum dynamics in strong, time-varying fields within the reduced density matrix approach. The corresponding weak-coupling GMEs and the generalised Redfield equations are presented there. These equations serve as a basis for subsequent applications and analysis of stochastic field-induced phenomena. Section 5 contains a simple implementation of our general approach which manifests the origin and basic features of strongly nonequilibrium phenomena described in the subsequent sections for more realistic models. The stochastically and periodically driven spin-boson model is discussed in section 6, including quantum stochastic resonance features. Section 7 is devoted to the phenomenon of noise-induced, ANM in quantum transport and to the analysis of dissipative quantum rectifiers. Concluding remarks are in section 8.

2. Quantum dynamics in stochastic fields

2.1. *Stochastic Liouville equation*

To begin, let us consider an arbitrary quantum system with a Hamilton operator $\hat{H}[\xi(t)]$ which depends on a classical, noisy parameter $\xi(t)$. This stochastic process $\xi(t)$ can take on either continuous or discrete values. Accordingly, the Hamiltonian $\hat{H}$ acquires, randomly in time, different operator values $\hat{H}[\xi(t)]$ which generally do not commute, i.e., $[\hat{H}[\xi(t)], \hat{H}[\xi(t')]] \neq 0$.

The posed problem is to average the corresponding quantum dynamics in the Liouville space, which is characterised by the Liouville-von-Neumann equation

$$\frac{d}{dt}\rho(t) = -i\mathcal{L}[\xi(t)]\rho(t), \tag{1}$$

for the density operator $\rho(t)$ over the realisations of noise $\xi(t)$. $\mathcal{L}[\xi(t)]$ in equation (1) stands for the quantum Liouville superoperator, $\mathcal{L}[\xi(t)](\cdot) = \frac{1}{\hbar}[\hat{H}[\xi(t)], (\cdot)]$. In other words, the objective is to evaluate the noise-averaged propagator

$$\langle S(t_0 + t, t_0)\rangle = \left\langle \mathcal{T} \exp\left[-i \int_{t_0}^{t_0+t} \mathcal{L}[\xi(\tau)]d\tau\right]\right\rangle, \tag{2}$$

where $\mathcal{T}$ denotes the time-ordering operator.

2.2. *Non-Markovian vs. Markovian discrete state fluctuations*

We specify this task for a discrete state noise with N states ξ_i (cf. figure 2). The noise is generally assumed to be a non-Markovian renewal process which is fully characterised by the set of transition probability densities $\psi_{ij}(\tau)$ for making random transitions within the time interval $[\tau, \tau + d\tau]$ from the state j to the state i. These probability densities are obviously positive and do obey the normalisation conditions

$$\sum_{i=1}^{N} \int_0^{\infty} {}_{ij}(\tau)d\tau = 1, \tag{3}$$

for all $j = 1, 2, \ldots, N$.

The subsequent residence time-intervals between jumps are assumed to be mutually uncorrelated. The residence time distribution (RTD) $\psi_j(\tau)$ in the

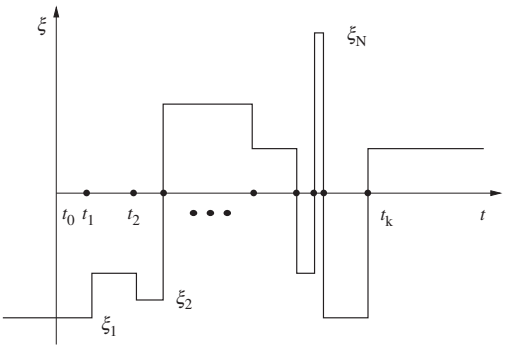

Figure 2. Typical trajectory of the considered process [105].

state j reads

$$ {}_{j}(\tau) = \sum_{i} \; {}_{ij}(\tau) = -\frac{d\Phi_j(\tau)}{d\tau}. \tag{4} $$

The survival probability $\Phi_j(\tau)$ of the state j follows then as

$$ \Phi_j(\tau) = \int_{\tau}^{\infty} \; {}_{j}(\tau)d\tau. \tag{5} $$

This constitutes the general description for continuous time random walk (CTRW) theory [106–109].

Several descriptions used for such simplest non-Markovian processes of the renewal type are worth mentioning. The approach in [110] with the time-dependent aging rates $k_{ij}(t)$ for the transitions from state j to state i corresponds to a particular choice

$$ {}_{ij}(\tau) := k_{ij}(\tau) \exp\left[-\sum_{i} \int_{0}^{\tau} k_{ij}(t)dt \right]. \tag{6} $$

The Markovian case corresponds to time-independent transition rates $k_{ij}(\tau) = const$. Any deviation of $\psi_{ij}(\tau)$ from the corresponding strictly exponential form which can be accounted for by introducing a time-dependence of the transition rates $k_{ij}(\tau)$ amounts to a non-Markovian behaviour.[1] Furthermore, the survival probability $\Phi_j(\tau)$ in the state j is determined by

$$ \Phi_j(\tau) = \exp\left[-\sum_{i=1}^{N} \int_{0}^{\tau} k_{ij}(t)dt \right] \tag{7} $$

and equation (6) can be recast as

$$ {}_{ij}(\tau) := k_{ij}(\tau)\Phi_j(\tau). \tag{8} $$

[1]This observation which can be traced back to [111] can be rationalised as follows. Let us consider a sojourn in the state j characterised by the survival probability $\Phi_j(\tau)$. The corresponding residence time interval $[0, \tau]$ can be arbitrarily divided into two pieces $[0, \tau_1]$ and $[\tau_1, \tau]$. If no memory effects are present, then $\Phi_j(\tau) = \Phi_j(\tau - \tau_1)\Phi_j(\tau_1)$. The only nontrivial solution of this latter functional equation which decays in time reads $\Phi_j(\tau) = \exp(-\gamma_j\tau)$, with $\gamma_j > 0$.

The introduction of time-dependent "aging" rates presents one possibility to describe the non-Markovian effects. It is not unique though. A different scheme follows by defining [112]:

$$_{ij}(\tau) := p_{ij}(\tau)\psi_j(\tau) \tag{9}$$

with $\sum_i p_{ij}(\tau) = 1$. The physical interpretation is as follows: The process stays in a state j for a random time interval characterised by the probability density $\psi_j(\tau)$. At the end of this time interval, it jumps into another state i with a generally time-dependent conditional probability $p_{ij}(\tau)$. Evidently, any process of the considered type can be interpreted in this way. By equating equations (8) and (9) and taking into account $\psi_j(\tau) := -d\Phi_j(\tau)/d\tau$ one can deduce that the approach in [110] can be reduced to that in [112] with the time-dependent transition probabilities

$$p_{ij}(\tau) = \frac{k_{ij}(\tau)}{\sum_i k_{ij}(\tau)} \tag{10}$$

and with the non-exponential probability densities $\psi_j(\tau)$ which follow as $\psi_j(\tau) = \gamma_j(\tau)\exp[-\int_0^\tau \gamma_j(t)dt]$ with $\gamma_j(\tau) := \sum_i k_{ij}(\tau)$.

The description of non-Markovian effects with the time-dependent transition probabilities $p_{ij}(\tau)$, is rather difficult to deduce immediately from the sample trajectories of an experimentally *observed* random process $\xi(t)$. The same holds true for the concept of time-dependent rates. These rates cannot be measured directly from the set of stochastic sample trajectories. On the contrary, the RTD $\psi_j(\tau)$ and the *time-independent* p_{ij} (with $p_{ii} := 0$) can routinely be deduced from sample trajectories measured, say, in a *single-molecular* experiment [113]. Figure 2 renders these assertions more obvious. The study of the statistics of the residence time-intervals allows one to obtain the corresponding probability densities $\psi_j(\tau)$ and, hence, the survival probabilities $\Phi_j(\tau)$. Furthermore, the statistics of the transitions from one state into all other states allows one to derive the corresponding conditional probabilities p_{ij}. From this primary information a complementary interpretation of experimental data in terms of time-dependent rates $k_{ij}(\tau)$ can readily be given as

$$k_{ij}(\tau) = -p_{ij}\frac{d\ln[\Phi_j(\tau)]}{d\tau}, \tag{11}$$

if one prefers to use this language to describe the non-Markovian effects. Moreover, the description with a constant set p_{ij} provides a consistent approach to construct the stationary realisations of $\xi(t)$, and thus to find the corresponding averaged quantum evolution [114].

2.3. *Averaging the quantum propagator*

The task of performing the noise-averaging of the quantum dynamics in equation (2) can be solved exactly due the piecewise constant character of the noise $\xi(t)$ [34, 49]. Let us consider the time-interval $[t_0, t]$ and take a frozen realisation of $\xi(t)$ assuming k switching events within this time-interval at the time-instants t_i,

$$t_0 < t_1 < t_2 < \cdots < t_k < t. \tag{12}$$

Correspondingly, the noise takes on the values $\xi_{j_0}, \xi_{j_1}, \ldots, \xi_{j_k}$ in the time sequel. Then, the propagator $S(t, t_0)$ reads

$$S(t, t_0) = e^{-i\mathcal{L}[\xi_{j_k}](t-t_k)} e^{-i\mathcal{L}[\xi_{j_{k-1}}](t_k-t_{k-1})} \cdots e^{-i\mathcal{L}[\xi_{j_0}](t_1-t_0)}. \tag{13}$$

Let us assume further that the process $\xi(t)$ has been *prepared* in the state j_0 at t_0. Then, the corresponding k-times probability density for such noise realisation is

$$P_k(\xi_{j_k}, t_k; \xi_{j_{k-1}}, t_{k-1}; \ldots; \xi_{j_1}, t_1 | \xi_{j_0}, t_0) = \Phi_{j_k}(t - t_k)\psi_{j_k j_{k-1}}(t_k - t_{k-1}) \cdots \psi_{j_1 j_0}(t_1 - t_0) \tag{14}$$

for $k \neq 0$ and $P_0(\xi_{j_0}, t_0) = \Phi_{j_0}(t - t_0)$ for $k = 0$. In order to obtain the noise-averaged propagator $\langle S(t|t_0, j_0)\rangle$ conditioned on such *nonstationary* initial noise preparation in the state j_0 one has to average (13) with the probability measure in (14) (for $k = \overline{0, \infty}$). This task can be easily done formally by use of the Laplace-transform [denoted in the following as $\tilde{A}(s) := \int_0^\infty \exp(-s\tau)A(\tau)d\tau$ for any time-dependent quantity $A(\tau)$]. The result for $\langle \tilde{S}(s|t_0, j_0)\rangle = \int_0^\infty \exp(-s\tau)\langle S(t_0 + \tau|t_0, j_0)\rangle d\tau$ reads [110, 114]

$$\langle \tilde{S}(s|t_0, j_0)\rangle = \sum_i \left(\tilde{A}(s)[I - \tilde{B}(s)]^{-1}\right)_{ij_0}, \tag{15}$$

where the matrix operators $\tilde{A}(s)$ and $\tilde{B}(s)$ reads in components

$$\tilde{A}_{kl}(s) := \delta_{kl} \int_0^\infty \Phi_l(\tau) e^{-(s+i\mathcal{L}[\xi_l])\tau} d\tau, \tag{16}$$

and

$$\tilde{B}_{kl}(s) := \int_0^\infty \quad {}_{kl}(\tau) e^{-(s+i\mathcal{L}[\xi_l])\tau} d\tau, \tag{17}$$

correspondingly, and I is the unity matrix.

To obtain the stationary noise averaging it is necessary to average (15) in addition over the stationary initial probabilities $p_{j_0}^{st}$. The averaging over the initial distribution alone is, however, not sufficient to arrive at the stationary noise-averaging in the case of non-Markovian processes since the noise realisations constructed in the way just described still remain non-stationary. This principal problem is rooted in the following observation. By preparing the quantum system at $t_0 = 0$ in a nonequilibrium state $\rho(0)$, the noise will be picked up at random in some initial state ξ_{j_0} with the probability $p_{j_0}^{st}$ (stationary noise). However, every time when we repeat the preparation of the quantum system in its initial state, the noise will already occupy a (random) state ξ_{j_0} for some unknown random time interval $\tau_{j_0}^*$ (setting a clock at $t_0 = 0$ sets the initial time for the quantum system, but not for the noise, which is assumed to start in the infinite past, cf. figure 2, where $\xi_{j_0} = \xi_1$ at $t_0 = 0$). Therefore, in a stationary setting, a proper averaging over this unknown time τ_j^* is necessary. The corresponding procedure implies that the mean residence time $\langle \tau_j \rangle$ is finite, $\langle \tau_j \rangle \neq \infty$, and yields a different RTD for the initial noise state, $\psi_j^{(0)}(\tau)$; namely, it is obtained as $\psi_j^{(0)}(\tau) = \Phi_j(\tau)/\langle \tau_j \rangle$ [115]. Only for Markovian processes where $\Phi_j(\tau)$ is strictly exponential, does $\psi_j^{(0)}(\tau)$ coincides with $\psi_j(\tau)$. Using this $\psi_j^{(0)}(\tau)$ instead of ${}_j(\tau)$ for the first sojourn in the corresponding state and for the *time-independent* set p_{ij}, the noise realisations become stationary [114–116]. The corresponding expression

for the quantum propagator averaged over such stationary noise realisations has been obtained in [114], cf. equations (25), (29) therein. In a slightly modified form it reads

$$\langle \tilde{S}(s)\rangle = \langle \tilde{S}(s)\rangle_{static} - \sum_{ij}\left(\tilde{C}(s) - \tilde{A}(s)[I - P\tilde{D}(s)]^{-1}P\tilde{A}(s)\right)_{ij}\frac{p_j^{st}}{\langle\tau_j\rangle}, \tag{18}$$

where $\langle \tilde{S}(s)\rangle_{static}$ is the Laplace-transform of the statically averaged Liouville propagator

$$\langle S(\tau)\rangle_{static} := \sum_k e^{-i\mathcal{L}[\xi_k]\tau}p_k^{st}, \tag{19}$$

$p_j^{st} = \lim_{t\to\infty} p_j(t)$ are the stationary probabilities which are determined by a system of linear algebraic equations [114, 116],

$$\frac{p_j^{st}}{\langle\tau_j\rangle} = \sum_n p_{jn}\frac{p_n^{st}}{\langle\tau_n\rangle}, \tag{20}$$

and P is the matrix of transition probabilities p_{ij} (''scattering matrix'' of the random process $\xi(t)$). Furthermore, the auxiliary matrix operators $\tilde{C}(s)$ and $\tilde{D}(s)$ in (18) read in components:

$$\tilde{C}_{kl}(s) := \delta_{kl}\int_0^\infty e^{-(s+i\mathcal{L}[\xi_l])\tau}\int_0^\tau \Phi_l(\tau')d\tau' d\tau \tag{21}$$

and

$$\tilde{D}_{kl}(s) := \delta_{kl}\int_0^\infty {}_l(\tau)e^{-(s+i\mathcal{L}[\xi_l])\tau}d\tau. \tag{22}$$

This very same averaging procedure can be applied to any system of linear stochastic differential equations.

2.3.1. Kubo oscillator. A prominent application of this general procedure is the noise-averaging procedure for the Kubo phase oscillator [48, 108]; reading

$$\dot{X}(t) = i\epsilon[\xi(t)]X(t). \tag{23}$$

This particular equation emerges in the theory of optical line shapes, in the NMR [32, 48], and for single-molecule spectroscopy [60]. It appears also naturally within our approach, see below, where $X(t)$ corresponds to a diagonal matrix element of the evolution operator of a quantum system with fluctuating eigenenergies. In the context of the stochastic theory of spectral line shapes [32, 48, 60], $\epsilon[\xi(t)]$ in equation (23) corresponds to a stochastically modulated frequency of quantum transitions between the levels of a ''two-state atom'', or transitions between the eigenstates of a spin 1/2 system.

The spectral line shape is determined via the corresponding stochastically averaged propagator of the Kubo oscillator as [48]

$$I(\omega) = \frac{1}{\pi}\lim_{\eta\to+0}\mathrm{Re}[\tilde{S}(-i\omega+\eta)]. \tag{24}$$

Note that the limit $\eta \to +0$ in equation (24) is necessary for the regularisation of the corresponding integral in the quasi-static limit $\langle \tau_j \rangle \to \infty$. Upon identifying $\mathcal{L}[\xi_k]$ with $-\epsilon_k$ in equation (18) we end up with

$$\langle \tilde{S}(s) \rangle = \sum_k \frac{p_k^{st}}{s - i\epsilon_k} - \sum_k \frac{1 - \tilde{\psi}_k(s - i\epsilon_k)}{(s - i\epsilon_k)^2} \frac{p_k^{st}}{\langle \tau_k \rangle} + \sum_{n,l,m} \frac{1 - \tilde{\psi}_l(s - i\epsilon_l)}{s - i\epsilon_l} \left(\frac{1}{I - P\tilde{D}(s)} \right)_{lm} p_{mn} \frac{1 - \tilde{\psi}_n(s - i\epsilon_n)}{s - i\epsilon_n} \frac{p_n^{st}}{\langle \tau_n \rangle}, \quad (25)$$

where $\tilde{D}_{nm}(s) = \delta_{nm} \tilde{\psi}_m(s - i\epsilon_m)$.[2] The corresponding line shape follows immediately from equation (25) by virtue of equation (24). This result presents a non-Markovian generalisation of the pioneering result by Kubo [48] for arbitrary N-state discrete Markovian processes. The generalisation consists in allowing for arbitrary non-exponential RTDs $\psi_k(\tau)$, or, equivalently, in accordance with equation (11) also for time-dependent transition rates $k_{ij}(\tau)$. This generalisation was put forward originally in [114] for a particular case, $p_j^{st} = \langle \tau_j \rangle / \sum_k \langle \tau_k \rangle$, which corresponds to an ergodic process with uniform mixing (meaning that in a long-time run each state j is visited equally often).

Let us next apply this result to the case of two-state non-Markovian noise with $p_{12} = p_{21} = 1$ and $p_{1,2}^{st} = \langle \tau_{1,2} \rangle / [\langle \tau_1 \rangle + \langle \tau_2 \rangle]$. Then, equation (25) yields after some simplifications:

$$\langle \tilde{S}(s) \rangle = \sum_{k=1,2} \frac{1}{s - i\epsilon_k} \frac{\langle \tau_k \rangle}{\langle \tau_1 \rangle + \langle \tau_2 \rangle} + \frac{(\epsilon_1 - \epsilon_2)^2}{(\langle \tau_1 \rangle + \langle \tau_2 \rangle)(s - i\epsilon_1)^2 (s - i\epsilon_2)^2} \times \frac{[1 - \tilde{\psi}_1(s - i\epsilon_1)][1 - \tilde{\psi}_2(s - i\epsilon_2)]}{1 - \tilde{\psi}_1(s - i\epsilon_1)\tilde{\psi}_2(s - i\epsilon_2)}. \quad (26)$$

With (26) in (24) one obtains the result for the corresponding spectral line shape which is equivalent to the one presented recently in [117] by use of a different method. It is reproduced within our treatment as a particular two-state limiting case. Moreover, in the simplest case of Markovian two-state fluctuations with $\tilde{\psi}_{1,2}(s) = 1/(1 + \langle \tau_{1,2} \rangle s)$ and with zero mean, $\langle \xi(t) \rangle = \langle \tau_1 \rangle \epsilon_1 + \langle \tau_2 \rangle \epsilon_2 = 0$, this result simplifies further to read

$$\langle \tilde{S}(s) \rangle = \frac{s + 2\chi}{s^2 + 2\chi s + \sigma^2}. \quad (27)$$

In (27), $\sigma = \sqrt{\langle \xi^2(t) \rangle} = |\epsilon_2 - \epsilon_1| \sqrt{\langle \tau_1 \rangle \langle \tau_2 \rangle} / (\langle \tau_1 \rangle + \langle \tau_2 \rangle)$ denotes the root mean squared (rms) amplitude of fluctuations. Moreover, $\chi = \nu/2 + i\sigma \sinh(b/2)$ is a complex frequency parameter, where $\nu = 1/\langle \tau_1 \rangle + 1/\langle \tau_2 \rangle$ is the inverse of the

[2]Note that the formal solution of another prominent problem of the first-order relaxation kinetics with a fluctuating rate, $\dot{p}(t) = -\Gamma[\xi(t)]\, p(t)$ follows immediately from (25) upon substitution $\epsilon_j \to i\Gamma_j$, see in [105] for some nontrivial non-Markovian examples and the corresponding discussion.

autocorrelation time of the considered process[3] which possesses the autocorrelation function $\langle \xi(t)\xi(t')\rangle = \sigma^2 \exp(-\nu|t-t'|)$. Furthermore, $b = \ln(\langle\tau_1\rangle/\langle\tau_2\rangle) = \ln|\epsilon_2/\epsilon_1|$ is an asymmetry parameter. The spectral line shape corresponding to (27) has been first obtained by Kubo [48]. It reads [48, 64],

$$I(\omega) = \frac{1}{\pi}\frac{\sigma^2\nu}{(\omega+\epsilon_1)^2(\omega+\epsilon_2)^2+\omega^2\nu^2}. \tag{28}$$

Moreover, the expression (27) can be readily inverted into the time domain. It is crucial that the corresponding averaged propagator $\langle S(t)\rangle$ of Kubo oscillator [70], i.e.,

$$\langle S(t)\rangle = e^{-\chi t}\Big[\cos(\sqrt{\sigma^2-\chi^2}\,t) + \frac{\chi}{\sqrt{\sigma^2-\chi^2}}\sin(\sqrt{\sigma^2-\chi^2}\,t)\Big], \tag{29}$$

is complex when the process $\xi(t)$ is asymmetric, $b \neq 0$. This correlates with the asymmetry of the corresponding spectral line shape, $I(-\omega) \neq I(\omega)$. Derived in a different form [118] (for a two-state Markovian process with a non-zero mean and in quite different notation) an expression equivalent to (29) is used in the theory of single-molecule spectroscopy [118–120]. For a symmetric dichotomous process (with $b = 0$) equation (29) reduces to the expression (6.10) (with $\omega_0 = 0$) in [47].

2.3.2. Averaged dynamics of two-level quantum systems exposed to two-state stochastic fields. The outlined non-Markovian stochastic theory of quantum relaxation can be exemplified for the instructive and relevant case of a two-level quantum system, reading

$$H(t) = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| + \frac{1}{2}\hbar\xi(t)(|1\rangle\langle 2| + |2\rangle\langle 1|), \tag{30}$$

which is driven by a two-state non-Markovian stochastic field $\xi(t) = \pm\Delta$ with identical RTDs, $\psi_1(\tau) = \psi_2(\tau) = \psi(\tau)$. This stochastic field causes (dipole) transitions between two states, $|1\rangle$ and $|2\rangle$, and is zero on average.

This archetype model exhibits a very rich behaviour. In particular, it allows one to study the problem of quantum decoherence of a two-state atom under the influence of two-state "$1/f^{\alpha}$" noises exhibiting long-range time-correlations with a power law decay (for $\psi(\tau)$ possessing a long-time algebraic tail, $\psi(\tau) \propto 1/\tau^{3-\alpha}$, $0 < \alpha < 1$) [121, 122]. It thus presents a prominent problem of general interest. Moreover, it relates to activities for solid state quantum computing [123]. It is convenient to express the Hamiltonian (30) in terms of Pauli matrices, $\hat{\sigma}_z := |1\rangle\langle 1| - |2\rangle\langle 2|$, $\hat{\sigma}_x := |1\rangle\langle 2| + |2\rangle\langle 1|$, $\hat{\sigma}_y := i(|2\rangle\langle 1| - |1\rangle\langle 2|)$ and the unity matrix $\hat{I}$,

$$H(t) = \frac{1}{2}\hbar\epsilon_0\hat{\sigma}_z + \frac{1}{2}\hbar\xi(t)\hat{\sigma}_x + \frac{1}{2}(E_1+E_2)\hat{I}, \tag{31}$$

where $\epsilon_0 = (E_1 - E_2)/\hbar$. Then, the dynamics of the density matrix of the quantum two-state quantum system can be given as $\rho(t) = \frac{1}{2}[\hat{I} + \sum_{i=x,y,z}\sigma_i(t)\hat{\sigma}_i]$ in terms of a classical spin dynamics (with components $\sigma_i(t) = \mathrm{Tr}(\rho(t)\hat{\sigma}_i)$) in a magnetic field.

[3]Note that throughout this work ν is the inverse of the autocorrelation time. It is equal to the sum of two rates.

This latter dynamics evolves on a Bloch sphere of unit radius (i.e., the (scaled) magnetic moment is conserved,[4] $|\vec{\sigma}(t)| = 1$). It reads,

$$\begin{aligned}\dot{\sigma}_x(t) &= -\epsilon_0\sigma_y(t),\\ \dot{\sigma}_y(t) &= \epsilon_0\sigma_x(t) - \xi(t)\sigma_z(t),\\ \dot{\sigma}_z(t) &= \xi(t)\sigma_y(t).\end{aligned} \tag{32}$$

The above theory can readily be applied to a noise averaging of three-dimensional system of linear differential equations (32) over arbitrary *stationary* realisations of $\xi(t)$. After some algebra, the following result is obtained [124] for the Laplace-transformed averaged difference of populations $\langle\sigma_z(t)\rangle = \langle\rho_{11}(t)\rangle - \langle\rho_{22}(t)\rangle$ with the initial condition $\sigma_z(0) = 1, \sigma_{x,y}(0) = 0$, i.e., the state "1" is populated initially with the probability one:

$$\langle\tilde{\sigma}_z(s)\rangle = \frac{s^2+\epsilon_0^2}{s(s^2+\Omega^2)} - \frac{2\Delta^2}{\tau s^2(s^2+\Omega^2)^2}\frac{\tilde{A}_{zz}(s)}{\tilde{B}_{zz}(s)}, \tag{33}$$

where

$$\begin{aligned}\tilde{A}_{zz}(s) = {}& \epsilon_0^2[1-\tilde{\psi}(s)]\big\{(\Omega^2-s^2)(1-\tilde{\psi}(s+i\Omega)\tilde{\psi}(s-i\Omega)) - 2i\Omega s[\tilde{\psi}(s+i\Omega)-\tilde{\psi}(s-i\Omega)]\big\}\\ & - \Delta^2 s^2[1+\tilde{\psi}(s)][1-\tilde{\psi}(s+i\Omega)][1-\tilde{\psi}(s-i\Omega)],\end{aligned} \tag{34}$$

$$\begin{aligned}\tilde{B}_{zz}(s) = {}& \epsilon_0^2[1-\tilde{\psi}(s)][1+\tilde{\psi}(s+i\Omega)][1+\tilde{\psi}(s-i\Omega)]\\ & + \Delta^2[1+\tilde{\psi}(s)](1-\tilde{\psi}(s+i\Omega)\tilde{\psi}(s-i\Omega)),\end{aligned}$$

and $\Omega := \sqrt{\epsilon_0^2+\Delta^2}$. Furthermore, τ is the mean residence time between the field's alternations. Note that for the considered initial condition, $\langle\sigma_x(t)\rangle = \langle\sigma_y(t)\rangle = 0$ for all times. For $\epsilon_0 = 0$ the result in (33)–(34) reduces to one for Kubo oscillator (26) with identical $\psi_{1,2}(\tau)$. Moreover, for the Markovian case, $\tilde{\psi}(s) = 1/(1+\tau s)$, equation (33) reduces to

$$\langle\tilde{\sigma}_z(s)\rangle = \frac{s^2+2\nu s+\nu^2+\epsilon_0^2}{s^3+2\nu s^2+(\Delta^2+\epsilon_0^2+\nu^2)s+\Delta^2\nu}, \tag{35}$$

where $\nu = 2/\tau$ is the inverse autocorrelation time. This latter result reproduces the result for the averaged populations $\langle\tilde{\rho}_{11}(s)\rangle = (1/s + \langle\tilde{\sigma}_z(s)\rangle)/2$ and $\langle\tilde{\rho}_{22}(s)\rangle = (1/s - \langle\tilde{\sigma}_z(s)\rangle)/2$ in [50, 51]. The same result (35) can also be reduced from a more general solution for the Markovian case with an asymmetric field of non-zero mean [54]. It possesses several remarkable features. First, the asymptotic difference between populations is zero, $\langle\sigma_z(\infty)\rangle = \lim_{s\to 0}(s\langle\tilde{\sigma}_z(s)\rangle) = 0$. In other words, the steady state populations of both energy levels equal 1/2, independently of the energy difference $\hbar\epsilon_0$. One can interpret this result in terms of a "temperature"

[4]This means that each and every stochastic trajectory runs on the Bloch sphere. The *averaged* Bloch vector $\langle\vec{\sigma}(t)\rangle$ becomes, however, contracted $|\langle\vec{\sigma}(t)\rangle| \le 1$, because $\langle\sigma_i(t)\rangle^2 \le \langle\sigma_i^2(t)\rangle$. Thus, the averaged density matrix $\langle\rho(t)\rangle$ is always positive in the considered model, cf. [47], independent of the particular model used for the stochastic driving $\xi(t)$.

T_σ of the (quasi-)spin system. This spin-temperature is formally introduced by using for the asymptotic distribution an Ansatz of the Boltzmann-Gibbs form, $\langle \rho_{nn}(\infty)\rangle = \exp[-E_n/k_B T_\sigma]/\sum_n \exp[-E_n/k_B T_\sigma]$. Then,[5]

$$T_\sigma := \frac{\hbar\epsilon_0}{k_B \ln(\langle\rho_{22}(\infty)\rangle/\langle\rho_{11}(\infty)\rangle)} \tag{36}$$

for two-level systems. In accord with this definition, the result of equal asymptotic populations, $\langle\rho_{22}(\infty)\rangle = \langle\rho_{11}(\infty)\rangle = 1/2$ can be interpreted in terms of an infinite temperature $T_\sigma = \infty$. This constitutes a general finding: a purely stochastic bath corresponds to an apparent infinite temperature [40, 41]. For this reason, such stochastic approaches to describe the relaxation process in open quantum systems is suitable only for sufficiently high temperatures $k_B T \gg \hbar|\epsilon_0|$ [40, 41]. An asymmetry of unbiased stochastic perturbations does not change this conclusion, see in [54]. Moreover, the relaxation to the steady state can be either coherent, or incoherent, depending on the noise strength and the autocorrelation time. In particular, an approximate analytical expression for the rate k of incoherent relaxation, $\langle\rho_{11}(t)\rangle = [1 + \exp(-kt)]/2$, has been obtained in a limit of small Kubo numbers, $K := \Delta/\nu \ll 1$, which corresponds to a weakly coloured noise [47, 49]. This analytical result reads [50, 51, 54]

$$k = \frac{\Delta^2 \nu}{\nu^2 + \epsilon_0^2} \tag{37}$$

and exhibits a resonance feature versus ν at $\nu = \epsilon_0$. A similar such resonance feature occurs also in the theory of NMR for a weakly coloured Gaussian noise [59]. Note that in [54] this notable result has been obtained for asymmetric fluctuations of the tunnelling coupling possessing a non-vanishing mean value $\langle\xi(t)\rangle \neq 0$. This corresponds to a quantum particle transfer between two sites of localisation which are separated by a fluctuating tunnelling barrier. A related problem with the inclusion of dissipation has been elaborated in [67] within a stochastically driven spin-boson model.

Yet another interesting solution can be obtained for $\langle\tilde{\sigma}_x(s)\rangle$ with the initial condition reading $\sigma_x(0) = 1$. The Laplace-transform of the solution is obtained as

$$\langle\tilde{\sigma}_x(s)\rangle = \frac{s^2 + \Delta^2}{s(s^2 + \Omega^2)} - \frac{2\Delta^2\epsilon_0^2\Omega^2}{\tau s^2 (s^2 + \Omega^2)^2} \frac{\tilde{A}_{xx}(s)}{\tilde{B}_{xx}(s)}, \tag{38}$$

where

$$\begin{aligned} \tilde{A}_{xx}(s) &= [1 - \tilde{\psi}(s)][1 - \tilde{\psi}(s + i\Omega)][1 - \tilde{\psi}(s - i\Omega)], \\ \tilde{B}_{xx}(s) &= \epsilon_0^2[1 + \tilde{\psi}(s)][1 - \tilde{\psi}(s + i\Omega)][1 - \tilde{\psi}(s - i\Omega)] \\ &\quad + \Delta^2[1 - \tilde{\psi}(s)](1 - \tilde{\psi}(s + i\Omega)\tilde{\psi}(s - i\Omega)). \end{aligned} \tag{39}$$

The physical relevance of this solution (38) is as follows. In a rotated quasi-spin basis, i.e., $\hat{\sigma}_x \to \hat{\sigma}_{z'}$, $\hat{\sigma}_z \to \hat{\sigma}_{x'}$, $\hat{\sigma}_y \to \hat{\sigma}_{y'}$, the considered problem becomes mathematically

[5]This is a standard definition of the temperature of a spin subsystem in NMR and similar areas [59]. It is used also to introduce the parlance of formally *negative* temperatures.

equivalent to the problem of the delocalisation of a quantum particle in a symmetric dimer with the tunnelling coupling ϵ_0 under the influence of a dichotomously fluctuating energy bias $\xi(t)$. Therefore, it describes the corresponding delocalisation dynamics and, in particular, allows one to determine whether this dynamics is coherent or incoherent, depending on the noise features.

For the Markovian case equation (38) reduces to[6]

$$\langle\tilde{\sigma}_x(s)\rangle = \frac{s^2 + \nu s + \Delta^2}{s^3 + \nu s^2 + (\Delta^2 + \epsilon_0^2)s + \epsilon_0^2\nu}. \tag{40}$$

Note that the denominators in equations (35) and (40) are different.[7] In a more general case of asymmetric Markovian noise, the corresponding denominator is a polynomial of 6th-order in s, see in [54]. In the considered case of symmetric noise it factorises into the product of two polynomials of 3rd-order, those in the denominators of equations (35) and (40). Thus, for a general initial condition the relaxation of a two-level quantum system exposed to a two-state Markovian field involves generally 6th-exponential terms. As a matter of fact, this seemingly simple, *exactly* solvable model can exhibit an unexpectedly complex behaviour even in the simplest Markovian case of a coloured noise driving. However, for certain initial conditions, as exemplified above, the general solution being a fraction of two polynomials of s simplifies to the results in equations (35) and (40).

In a general case of non-Markovian noise, the analytical solutions in equations (33) and (38) can be inverted to the time domain numerically by use of a numerical Laplace inversion procedure such as the one detailed in [125].

2.4. *Projection operator method: a primer*

Next we shall introduce the reader, following [126], into the projection operator technique. We elucidate this scheme by addressing an example that is of physical interest in its own right.

Let us consider the somewhat more general dynamics,

$$\begin{aligned}\frac{d\vec{\sigma}(t)}{dt} &:= \begin{pmatrix}\dot{\sigma}_x(t)\\ \dot{\sigma}_y(t)\\ \dot{\sigma}_z(t)\end{pmatrix} = \begin{pmatrix}0 & -\epsilon(t) & 0\\ \epsilon(t) & 0 & -\Delta(t)\\ 0 & \Delta(t) & 0\end{pmatrix}\begin{pmatrix}\sigma_x(t)\\ \sigma_y(t)\\ \sigma_z(t)\end{pmatrix}\\ &:= \hat{B}(t)\vec{\sigma}(t),\end{aligned} \tag{41}$$

[6]The corresponding dynamics also exhibits a resonance feature versus ν in a certain limit [56].
[7]A remarkable feature is, however, that both corresponding secular cubic equations have the *same* discriminant, $D(\Delta, \nu, \epsilon_0) = 0$, separating the domains of complex and real roots. Hence, the transition from a coherent relaxation (complex roots are present) to an incoherent relaxation (real roots only) occurs at the same values of noise parameters, independently of the initial conditions. The corresponding phase diagram separating regimes of coherent and incoherent relaxation (judging from the above criterion) has been found in [56]. It must be kept in mind, however, that the weights of the corresponding exponentials are also of importance for the character of relaxation process. These weights naturally depend on the initial conditions.

and let us pose the question: How can we extract a single, closed equation for the evolution of $\sigma_z(t)$ (without any approximation) for an arbitrary time-dependence of the parameters governing the driven quantum dynamics? The use of a projection operator method provides an elegant way to solve this problem [126]. The key idea is to project the whole dynamics onto a corresponding subspace of reduced dimensionality by using a projection operator $\mathcal{P}$ with the idempotent property $\mathcal{P}^2 = \mathcal{P}$. In the present case, the choice of this projection operator follows naturally as:

$$\mathcal{P}\begin{pmatrix}\sigma_x(t)\\ \sigma_y(t)\\ \sigma_z(t)\end{pmatrix} = \begin{pmatrix}0\\ 0\\ \sigma_z(t)\end{pmatrix} := \vec{\sigma}_0(t). \tag{42}$$

The use of this projection operator allows one to split the whole dynamics into the "relevant" one $\vec{\sigma}_0(t)$, and a remaining, "irrelevant", $\vec{\mu}(t)$, part, respectively; i.e., $\vec{\sigma}(t) \equiv \mathcal{P}\vec{\sigma}(t) + (1-\mathcal{P})\vec{\sigma}(t) := \vec{\sigma}_0(t) + \vec{\mu}(t)$ by applying $\mathcal{P}$ and the complementary projection operator $1-\mathcal{P}$ to equation (41). From the resulting system of two coupled linear equations for $\vec{\sigma}_0(t)$ and $\vec{\mu}(t)$, i.e.,

$$\begin{aligned}\frac{d\vec{\sigma}_0(t)}{dt} &= \mathcal{P}\hat{\boldsymbol{B}}(t)\vec{\sigma}_0(t) + \mathcal{P}\hat{\boldsymbol{B}}(t)\vec{\mu}(t),\\ \frac{d\vec{\mu}(t)}{dt} &= (1-\mathcal{P})\hat{\boldsymbol{B}}(t)\vec{\sigma}_0(t) + (1-\mathcal{P})\hat{\boldsymbol{B}}(t)\vec{\mu}(t),\end{aligned} \tag{43}$$

a single integro-differential equation for $\vec{\sigma}_0(t)$ follows, reading:

$$\begin{aligned}\frac{d\vec{\sigma}_0(t)}{dt} = \mathcal{P}\hat{\boldsymbol{B}}(t)\vec{\sigma}_0(t) &+ \int_0^t \mathcal{P}\hat{\boldsymbol{B}}(t)\mathcal{T}\exp\left(\int_{t'}^t d\tau(1-\mathcal{P})\hat{\boldsymbol{B}}(\tau)\right)(1-\mathcal{P})\hat{\boldsymbol{B}}(t')\vec{\sigma}_0(t')dt'\\ &+ \mathcal{P}\hat{\boldsymbol{B}}(t)\mathcal{T}\exp\left(\int_0^t d\tau(1-\mathcal{P})\hat{\boldsymbol{B}}(\tau)\right)\vec{\mu}(0).\end{aligned} \tag{44}$$

The exponential matrix operations in (44) can be done explicitly without any approximation, yielding the *exact* closed equation for $\sigma_z(t)$ [126], reading[8]

$$\begin{aligned}\dot{\sigma}_z(t) = &-\int_0^t \Delta(t)\Delta(t')\cos[\zeta(t,t')]\sigma_z(t')dt'\\ &+ \Delta(t)\sin[\zeta(t,0)]\sigma_x(0) + \Delta(t)\cos[\zeta(t,0)]\sigma_y(0).\end{aligned} \tag{45}$$

In equation (45), the time-dependent phase

$$\zeta(t,t') = \int_{t'}^t \epsilon(\tau)d\tau \tag{46}$$

is introduced which is a functional of the time-varying parameter $\epsilon(t)$. The projection of the entire dynamics onto some subspace typically entails memory effects.

[8]Within the path-integral approach, the same equation can be derived from a non-interacting blip approximation (NIBA) result of the dissipative spin-boson model [132] by putting formally therein the strength of the system-bath coupling to zero. Astonishingly enough, the NIBA turns out to provide the exact result for this singular limit of zero-dissipation.

Put differently, a non-locality in time emerges for the reduced space dynamics. Moreover, an explicit dependence on the initial conditions in the "irrelevant" subspace is necessarily present.

3. Two-state quantum dynamics in periodic fields

Let us illustrate the practical usefulness of the *exact* equation (45) by its application to a quantum dynamics occurring in strong time-periodic fields. Towards this goal, we consider a quantum two-state tunnelling system, where the two states $|1\rangle$ and $|2\rangle$ correspond to the two sites of charge localisation (i.e., we work in the "tunnelling" representation) and $\Delta = const$ corresponds to the tunnelling matrix element. This charge dynamics is driven by a periodic electric field of frequency Ω which results in a periodic modulation of the energy bias between two localised states $\epsilon(t) = \epsilon_0 + A\cos(\Omega t)$ [3]. We assume that the particle is prepared initially on the site "1" at $t = 0$, i.e., $\sigma_z(0) = 1$ and $\sigma_x(0) = \sigma_y(0) = 0$. Further, one assumes that the frequency of external field is rather high, $\Omega \gg \Delta$ and we consider the correspondingly averaged dynamics $\langle\sigma_z(t)\rangle_\Omega$ using the high-frequency decoupling approximation $\langle\cos[\zeta(t,t')]\sigma_z(t')\rangle_\Omega \approx \langle\cos[\zeta(t,t')]\rangle_\Omega\langle\sigma_z(t')\rangle_\Omega$ [83]. Using equation (46) and the well-known identity $\exp(iz\sin\theta) = \sum_{n=-\infty}^{\infty} J_n(z)\exp(in\theta)$ ($J_n(z)$ denotes the Bessel function of the first kind) the high-frequency approximation in equation (45) yields

$$\langle\dot{\sigma}_z(t)\rangle_\Omega = -\Delta^2 \int_0^t \Gamma(t-t')\langle\sigma_z(t')\rangle_\Omega dt' \tag{47}$$

with the kernel $\Gamma(t) = \sum_{n=-\infty}^{\infty} J_n^2(A/\Omega)\cos[(\epsilon_0 + n\Omega)t]$. This latter equation can be solved by the use of the Laplace-transform. For $\tilde{\sigma}_z(s) := \int_0^t \exp(-st)\langle\sigma_z(t)\rangle_\Omega dt$ one obtains

$$\tilde{\sigma}_z(s) = \frac{1}{s}\,\frac{1}{1 + \Delta^2 \sum_{n=-\infty}^{\infty} (J_n^2(A/\Omega))/(s^2 + (\epsilon_0 - n\Omega)^2)}\ . \tag{48}$$

From this relation now follow some key-results.

3.1. *Coherent destruction of tunnelling*

The formal inversion of the result in equation (48) into the time domain reads

$$\langle\sigma_z(t)\rangle_\Omega = \sum_{j=0,\,\pm1,\,\pm2,\,\ldots} c_j \exp(i\omega_j t), \tag{49}$$

where $\omega_j = is_j > 0$ are the poles s_j of equation (48). From the quasi-periodic character of the driven dynamics it follows that all these poles lie on the imaginary axis in complex conjugated pairs. Therefore, $\omega_{-j} = -\omega_j$ and $c_{-j} = c_j^*$. Although there appears an infinite number of poles, only few of them contribute significantly in the regimes of interest.

Let us consider the case of symmetric two-level system (TLS), $\epsilon_0 = 0$. Then, the approximate solution reads (only the term with $n = 0$ in the sum in equation (48) contributes significantly in the high-frequency limit $\Delta/\Omega \to 0$)

$$\langle\sigma_z(t)\rangle_\Omega = \cos(\Delta_{tun} t), \tag{50}$$

where $\Delta_{tun} = \Delta|J_0(A/\Omega)|$ is the renormalised tunnelling frequency. When the amplitude A of the high-frequency driving is chosen to obey $J_0(A/\Omega) = 0$, the tunnelling dynamics is brought (within this high-frequency approximation) to a complete standstill. This constitutes the celebrated phenomenon of coherent destruction of tunnelling (CDT) [127, 128] which attracted much attention and generated many applications over recent years, see e.g., in [3, 4] and references therein.

3.2. *Driving-induced tunnelling oscillations (DITO)*

Let us consider now the case of a large energy bias $\epsilon_0 \gg \Delta$. In the absence of driving, the particle remains essentially localised on the site "1", $\sigma_z(t) \approx 1$, as can be deduced from the well-known exact solution $\sigma_z(t) = [\epsilon_0^2 + \Delta^2 \cos(\sqrt{\epsilon_0^2 + \Delta^2}t)]/[\epsilon_0^2 + \Delta^2]$. When, however, a high-frequency driving $\Omega \gg \Delta$ is applied such that the resonance condition $n\Omega = \sqrt{\epsilon_0^2 + \Delta^2} \approx \epsilon_0$ is approximately fulfilled, large amplitude tunnelling oscillations in equation (50) can be induced with a tunnelling frequency $\Delta_{tun} = \Delta|J_n(A/\Omega)|$. This phenomenon of driving-induced tunnelling oscillations (DITO), being opposite to CDT has been revealed in [87, 129, 130]. It has recently been verified and observed experimentally [130]. This DITO phenomenon is illustrated in figure 3 for an "exotic" 5-photon ($n = 5$) resonance case where the precise numerical solution of driven TLS dynamics using equation (41) and the approximation in equation (50) with $\Delta_{tun} = \Delta|J_n(A/\Omega)|$ are plotted for the following set of parameters: $\Delta = 0.1$, $\epsilon_0 = 20$, $A = 24$, $\Omega = 3.9$ or $\Omega = 4.0$. For $\Omega = 3.9$ the dynamics is almost localised exhibiting small-amplitude oscillation – cf. dotted line near $\sigma_z(t) = 1$ which is barely visible in figure 3a but becomes clearly seen in figure 3b due to a better resolution on a different scale. A relatively small change of the periodic-field frequency chosen to match the resonance condition $5\Omega = \epsilon_0$ induces large-amplitude tunnelling oscillations which are nicely described on the long-time-scale by the approximation in equation (50) with $\Delta_{tun} = \Delta|J_5(A/\Omega)|$. It cannot be distinguished from the precise numerical solution in figure 3a. The frequency of these oscillations is controlled by both the bare tunnelling frequency Δ and the field amplitude A. It is worth mentioning that DITO seems to be close in spirit to the famous Rabi oscillations [131] (an interpretation given in [130]), but are in fact by no means identical

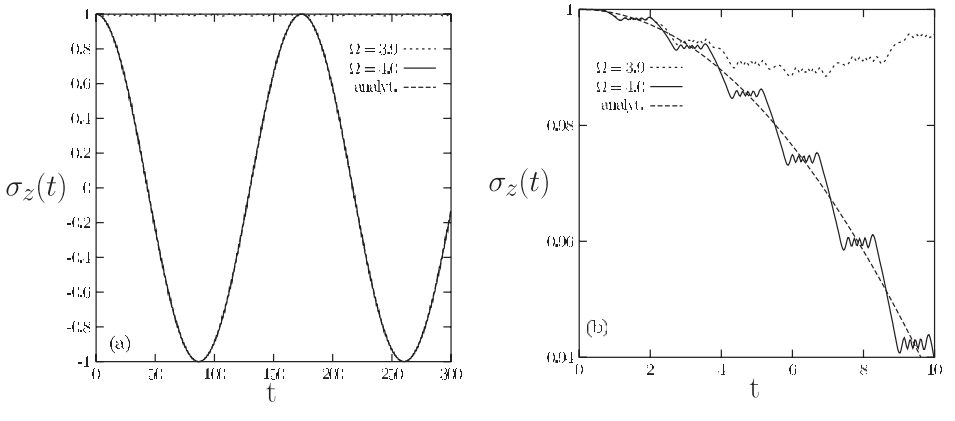

Figure 3. Driving-induced tunnelling oscillations.

with those. Rabi oscillations correspond usually to a particular case of a small-amplitude, $A \ll \Omega$, resonant driving, $\Omega = \sqrt{\Delta^2 + \epsilon_0^2}$. For $\epsilon_0 = 0$, the corresponding problem is equivalent (in a rotated quasi-spin basis, $\hat{\sigma}_x \to \hat{\sigma}_{z'}$, $\hat{\sigma}_z \to \hat{\sigma}_{x'}$, $\hat{\sigma}_y \to \hat{\sigma}_{y'}$, and with different initial conditions) to the resonant dipole excitation of a two-state atom with eigenfrequency $\omega_0 = \Delta$. In such a case, the frequency of Rabi oscillations ω_R is determined approximately by the driving *amplitude*, i.e., $\omega_R \approx A$ [3, 161]. This presents the most remarkable, characteristic feature of Rabi oscillations. The DITO frequency presents rather a driving-renormalised tunnelling frequency as in the case of CDT. The coarse-grained character of the result in equation (50) is illustrated in figure 3b on a short-time-scale in comparison with the precise numerical solution of the driven dynamics. This latter one exhibits step-like transitions with a number of oscillations on each step. The number of oscillations corresponds to the number of emitted (absorbed) photons. With the increase of n, the ''steps'' become longer and sharper. In order to make a further ''step'' in the transfer of population the two level system awaits for the next portion of n photons to be emitted, or absorbed to match the resonance condition $n\Omega = \epsilon_0$ (a quasi-classical interpretation of the numerically observed step feature).

4. Dissipative quantum dynamics in strong time-dependent fields

4.1. *General formalism*

Without loss of generality we consider a N-level, driven quantum system characterised by a time-dependent Hamilton operator $H_S(t)$ and which interacts V_{SB} with a thermal bath characterised by a Hamilton operator H_B. The system-bath interaction is assumed here to be generally also time-dependent. It is characterised by the Hamilton operator $V_{SB}(t)$ which depends both on the (relevant) variables of the system of interest and on the thermal bath variables. The total Hamiltonian $H(t)$ thus reads

$$H(t) = H_S(t) + V_{SB}(t) + H_B. \tag{51}$$

The dynamics of the density operator $\rho(t)$ of the total system is then governed by the corresponding Liouville-von-Neumann equation, cf. equation (1). Furthermore, the reduced density operator of interest is obtained by performing a partial trace of $\rho(t)$ over the bath variables, i.e., $\rho_S(t) = \mathrm{Tr}_B \rho(t)$. The average $\langle A \rangle$ of any operator A which depends on the variables of the system of interest can be calculated as the corresponding trace over the system variables, i.e., $\langle A \rangle = \mathrm{Tr}_S(\rho_S(t)A)$. The reduced density operator $\rho_S(t)$, which also depends on the initial preparation scheme, thus contains all the necessary information required to describe the time-evolution of the system of interest. The main task consists in obtaining a tractable closed equation of motion for $\rho_S(t)$. This can be achieved by applying to $\rho(t)$ a properly chosen projection operator Π, which projects the whole dynamics onto the subspace of the considered quantum system, thereby accounting indirectly for the ''irrelevant'' bath variables, i.e. $\rho_S(t) = \Pi\rho(t)$. A proper choice for the projection operator with the idempotent property, $\Pi^2 = \Pi$, is $\Pi := \rho_B \mathrm{Tr}_B$ [22–24], where $\rho_B = \exp(-\beta H_B)/Z_B$ is the equilibrium density operator of the bath; $Z_B = \mathrm{Tr}_B \exp(-\beta H_B)$ is the corresponding partition sum, and $\beta = 1/(k_B T)$ denotes the inverse temperature. Then, $\rho(t)$

can identically be split as $\rho(t) \equiv \rho_B \otimes \rho_S(t) + \eta(t)$, where $\eta(t) = Q\rho(t)$ represents a cross-correlation term. Here, $Q := 1 - \Pi$ is the complementary projection operator with the properties $Q\Pi = \Pi Q = 0, Q^2 = Q$. By applying Π and Q to the Liouville-von-Neumann equation for $\rho(t)$, two coupled linear operator equations for $\rho_S(t)$ and $\eta(t)$ can be obtained, respectively, which in turn yield a single closed equation for $\rho_S(t)$ after having eliminated the part $\eta(t)$. The formally *exact* equation for the reduced density operator, thus reads

$$\dot{\rho}_S(t) = -iL_S(t)\rho_S(t) - \int_0^t \Gamma(t,t')\rho_S(t')dt' + I_0(t), \tag{52}$$

where

$$\Gamma(t,t') = \mathrm{Tr}_B[L_{SB}(t)S_{S+B}(t,t')QL_{SB}(t')\rho_B] \tag{53}$$

denotes the memory kernel. In equation (53),

$$S_{S+B}(t,t') = \mathcal{T}\exp\left\{-i\int_{t'}^t [L_S(\tau) + L_B + QL_{SB}(\tau)]d\tau\right\} \tag{54}$$

is a Liouvillian propagator. Furthermore, $L_S(t)(\cdot) = [\tilde{H}_S(t),(\cdot)]/\hbar$, $L_B(\cdot) = [H_B,(\cdot)]/\hbar$, $L_{SB}(t)(\cdot) = [\tilde{V}_{SB}(t),(\cdot)]/\hbar$ are the corresponding Liouville operators, where $\tilde{H}_S(t) := H_S(t) + \langle V_{SB}(t)\rangle_B$ is the renormalised Hamiltonian of the dynamical system and $\tilde{V}_{SB}(t) := V_{SB}(t) - \langle V_{SB}(t)\rangle_B$ is the correspondingly re-defined system-bath coupling.[9] Moreover, $I_0(t)$ in equation (52)

$$I_0(t) = -i\mathrm{Tr}_B\big(L_{SB}(t)S_{S+B}(t,0)\mu(0)\big) \tag{55}$$

constitutes the initial correlation term, sometimes also termed "initial value term".

Note that the GME (52)–(55) is still exact in the subspace of the quantum system for a quantum evolution started at $t_0 = 0$, i.e., no approximations have been invoked so far [26, 27, 133]. Generally, a reduced quantum evolution contains some dependence on the initial conditions $\mu(0)$ in the irrelevant subspace. We note, however, that for a factorised (uncorrelated) initial preparation $\rho(0) = \rho_B \otimes \rho_S(0)$ ($\mu(0) = 0$) this initial correlation term vanishes identically, i.e., $I_0(t) = 0$. This standard class of initial preparations will be assumed in the following.

4.1.1. Weak-coupling approximation. In the second-order approximation with respect to the system-bath coupling $V_{SB}(t)$ (the so termed weak-coupling limit) one sets $L_{SB}(t) \to 0$ in $S_{S+B}(t,t')$, equation (54). Moreover, let us assume a factorising

[9]This issue deserves to be commented on in further detail: The generalised quantum thermal forces acting on the system from the bath should be on average unbiased. This implies that the *thermal* average $\langle\cdots\rangle_B := \mathrm{Tr}_B(\rho_B\ldots)$ of a properly defined system-bath coupling, $\langle\tilde{V}_{SB}(t)\rangle_B := \mathrm{Tr}_B(\rho_B\tilde{V}_{SB}(t))$, should be zero, i.e., $\langle\tilde{V}_{SB}(t)\rangle_B = 0$. For this reason, the systematic, *mean-field* like contribution $\langle V_{SB}(t)\rangle_B$ of the thermal "force" should be separated from the very beginning and be included in $\tilde{H}_S(t)$ without change of the Hamiltonian of the *total* system. Obviously, this can *always* be achieved. This formal renormalisation is *always* assumed in the following (with "tilde" omitted when applicable).

form of the system-bath coupling $V_{SB}(t) = \frac{1}{2}\sum_\alpha \kappa_\alpha(t)\hat{\gamma}_\alpha\hat{\xi}_\alpha + h.c.$ where $\hat{\gamma}_\alpha$ denote some system operators, $\hat{\xi}_\alpha$ are the bath operators, and $\kappa_\alpha(t)$ are the coupling strength functions. The complete set $\hat{\gamma}_\alpha$ is assumed to be closed under commutation relations: $[\hat{\gamma}_\alpha, \hat{\gamma}_\beta] = \sum_\delta \epsilon_{\alpha\beta\delta}\hat{\gamma}_\delta$ with $\epsilon_{\alpha\beta\delta}$ being some structural constants defining a corresponding Lie algebra with generators $\hat{\gamma}_\alpha$. The Hamiltonian $H_S(t)$ is represented as a linear superposition

$$H_S(t) = \frac{1}{2}\sum_\alpha b_\alpha(t)\hat{\gamma}_\alpha + h.c.$$

in the corresponding algebra. For N-level quantum systems the following set of operators is conveniently used. It is given (here $\alpha := (n, m)$) by the set of operators $\hat{\gamma}_{nm} := |n\rangle\langle m|$ (they correspond to the elements of corresponding Liouville space). Here, the ket-vectors $|n\rangle$ provide an orthonormal vector basis with the scalar product $\langle n|m\rangle = \delta_{nm}$ in the corresponding Hilbert space of the considered N-level quantum system. The representation of the system Hamiltonian in this discrete basis reads

$$H_S(t) = \sum_{nm} H_{nm}(t)\hat{\gamma}_{nm}, \tag{56}$$

with $H_{nm}(t) = H^*_{mn}(t)$. It is evident that any quantum system with a discrete number of states can be represented in this way. The system-bath coupling can be chosen in the form

$$V_{SB}(t) = \sum_{nm} \kappa_{nm}(t)\hat{\gamma}_{nm}\hat{\xi}_{nm}, \tag{57}$$

with $\kappa_{mn}(t) = \kappa^*_{nm}(t)$ and $\hat{\xi}_{mn} = \hat{\xi}^\dagger_{nm}$. Moreover, the dissipative operator kernel in equation (52) reads in the given approximation:

$$\begin{aligned}\Gamma(t, t')(\cdot) = \sum_{n,n',m,m'} \kappa_{nn'}(t)\kappa_{mm'}(t')\Big\{ & K_{nn'mm'}(t-t')\Big[\hat{\gamma}_{nn'}, S(t, t')\hat{\gamma}_{mm'}(\cdot)\Big] \\ & - K^*_{n'nm'm}(t-t')\Big[\hat{\gamma}_{mn'}, S(t, t')(\cdot)\hat{\gamma}_{mm'}\Big]\Big\},\end{aligned} \tag{58}$$

where

$$S(t, t') = \mathcal{T}\exp\left\{-i\int_{t'}^{t} L_S(\tau)d\tau\right\} \tag{59}$$

is the Liouville evolution operator of the physical system under consideration. Note that it does include the external, time-dependent field influences exactly. Moreover,

$$K_{nn'mm'}(t) := \frac{1}{\hbar^2}\langle\hat{\xi}_{nn'}(t)\hat{\xi}_{mm'}\rangle_B = K^*_{m'mn'n}(-t), \tag{60}$$

is the autocorrelation tensor of the thermal force operators $\hat{\xi}_{nn'}(t) := e^{iH_B t/\hbar}\hat{\xi}_{nn'}e^{-iH_B t/\hbar}$. An expression formally similar to equation (58) has been obtained first, for a particular case of a spin 1/2 system (and for a time-independent system-bath coupling) in [24]. For the reduced density matrix, $\rho_{nm}(t) := \langle n|\rho_S(t)|m\rangle$ the following GME follows:

$$\dot{\rho}_{nm}(t) = -i\sum_{n'm'} L_{nmn'm'}(t)\rho_{n'm'}(t) - \sum_{n'm'}\int_0^t \Gamma_{nmn'm'}(t, t')\rho_{n'm'}(t')dt', \tag{61}$$

where $L_{nmn'm'}(t) = \frac{1}{\hbar}[H_{nn'}(t)\delta_{mm'} - H_{m'm}(t)\delta_{nn'}]$ is the Liouville superoperator, written in the supermatrix representation and the corresponding memory kernels read

$$\begin{aligned}\Gamma_{nmn'm'}(t,t') = \sum_{kk'} \Big\{ & \kappa_{nk'}(t)\kappa_{kn'}(t')K_{nk'kn'}(t-t')U_{k'k}(t,t')U^*_{mm'}(t,t') \\ & + \kappa_{k'm}(t)\kappa_{m'k}(t')K^*_{mk'km'}(t-t')U_{nn'}(t,t')U^*_{k'k}(t,t') \\ & - \kappa_{nk'}(t)\kappa_{m'k}(t')K^*_{k'nkm'}(t-t')U_{k'n'}(t,t')U^*_{mk}(t,t') \\ & - \kappa_{k'm}(t)\kappa_{kn'}(t')K_{k'mkn'}(t-t')U_{nk}(t,t')U^*_{k'm'}(t,t') \Big\}, \end{aligned} \tag{62}$$

where $U_{mm'}(t,t') := \langle m|\mathcal{T}\exp\{-\frac{i}{\hbar}\int_{t'}^{t} H_S(\tau)d\tau\}|m'\rangle$ is the evolution operator of the considered quantum system in the Hilbert space. This result presents the most general form of weak-coupling GME in arbitrary external fields. Generalised master equations of a similar form have been derived before, by making use of different methods and in different notations in [64, 66, 82].[10] The kernel (62) satisfies two important properties which must be strictly obeyed; these are (i):

$$\Gamma_{nmn'm'}(t,t') = \Gamma^*_{mnm'n'}(t,t')$$

(imposed by the requirement that $\rho_S(t)$ must be Hermitian, $\rho_S(t) = \rho_S^\dagger(t)$), and (ii):

$$\sum_n \Gamma_{nnn'm'}(t,t') = 0$$

(conservation of probability, $\mathrm{Tr}_S\,\rho_S(t) = 1$ for all times).

This driven GME (61) presents our "working horse" that will be used frequently for the discussion of various applications detailed below.

4.1.2. Markovian approximation: Generalised Redfield Equations. The integro-differential equations (61)–(62) are, notably, non-local in time, i.e., they describe a so-termed "non-Markovian" quantum dynamics. This non-locality in time makes their practical use rather cumbersome. A corresponding Markovian approximation, which renders a description that is local in time, is therefore of great use in practice, if it can be justified on physical grounds. There are several ways to obtain such a Markovian approximation. The most popular one is to perform a back propagation, i.e., $\rho_S(t') = S^{-1}(t,t')\rho_S(t) + O(\kappa^2)$, in the kernel of GME making use of the Liouville evolution operator $S(t,t')$ of the dynamical subsystem. The corresponding master equation for the reduced density matrix, which constitutes the generalisation of the well-known Redfield equations [135] to the case of driven, open quantum systems reads:

$$\dot{\rho}_{nm}(t) = -i\sum_{n'm'} L_{nmn'm'}(t)\rho_{n'm'}(t) - \sum_{n'm'} R_{nmn'm'}(t)\rho_{n'm'}(t), \tag{63}$$

[10]For a periodic driving, the field influence on the relaxation kernel can alternatively be taken into account applying the corresponding Floquet basis for periodically driven quantum dynamics. This has been done in [84, 95]. Our approach is valid, however, for arbitrary time-dependence.

with the explicit *time-dependent* relaxation tensor

$$R_{nmn'm'}(t) = \sum_{kk'} \int_0^t \Big\{ \sum_l [\kappa_{nl}(t)\kappa_{kk'}(t') K_{nlkk'}(t-t') U_{lk}(t,t') U^*_{n'k'}(t,t') \delta_{mm'} + \kappa_{lm}(t)\kappa_{kk'}(t') K^*_{mlk'k}(t-t') U_{m'k}(t,t') U^*_{lk'}(t,t') \delta_{nn'}] - \kappa_{nn'}(t)\kappa_{kk'}(t') K^*_{n'nk'k}(t-t') U_{m'k}(t,t') U^*_{mk'}(t,t') - \kappa_{m'm}(t)\kappa_{kk'}(t') K_{m'mkk'}(t-t') U_{nk}(t,t') U^*_{n'k'}(t,t') \Big\} dt'. \quad (64)$$

This relaxation tensor satisfies two important relations, namely, $R_{nmn'm'}(t) = R^*_{mnm'n'}(t)$ ($\rho_S(t)$ is Hermitian), and $\sum_n R_{nnn'm'}(t) = 0$ (imposed by the conservation of probability). Notable, the upper limit of integral in (64) is here the actual evolution time t (instead of ∞) – this feature softens already the well-known problem which relates to a possible violation of positivity at initial time-scales of the quantum evolution [136] for Redfield equations for certain initial conditions.[11] Upon neglecting (setting to zero) the influence of external time-dependent fields in the relaxation tensor, by using the basis of *eigenstates* of *time-independent* H_S, and setting $t \to \infty$ in (64), we recover the commonly known form of the Redfield relaxation tensor.

It must be stressed that the physical nature of the thermal bath operators was up to now still not specified. Those can be either be of bosonic, fermionic nature, or also describe a spin bath [134]. The corresponding autocorrelation tensor (60) has to be calculated for every particular microscopic model. We next address within this methodology several physical applications.

5. Application I: Quantum relaxation in driven, dissipative two-level systems

Let us consider a two-level quantum system with time-dependent eigenenergy levels,[12]

$$H_S(t) = \Big[E_1^{(0)} + \tilde{E}_1(t)\Big]|1\rangle\langle 1| + \Big[E_2^{(0)} + \tilde{E}_2(t)\Big]|2\rangle\langle 2|, \quad (65)$$

[11]This problem can be resolved by the so-called slippage of the initial conditions, see in [137–139]. Moreover, within the weak-coupling approximation the effect of dissipation should be consistently taken into account to the second-order of the system-bath coupling only; i.e., in the solutions of Redfield equations (rather than in the relaxation kernels only). The dissipation-induced frequency shifts (i.e. the Lamb shifts at $T = 0$) should also be very small (compared to the corresponding eigenfrequencies of quantum evolution in the absence of dissipation). Otherwise, the theory needs to be renormalised. Notwithstanding these essential restrictions, the Redfield equations provide one of the most widely used tools to describe open quantum systems in many areas of physics and physical chemistry [3, 4, 9, 59, 140–143].

[12]These levels can correspond, e.g., to spatially separated localisation sites of a transferring (excess) electron in a protein [11]. If such electronic states possess very different dipole moments (the difference can reach 50 D [144]), an external time-dependent electric field will modulate the energy difference in time due to the Stark effect. Such electric field dependence of the electronic energy levels can be very strong [144, 145]. A large modulation of the local electric field can be induced, e.g., due attachment/detachment of an ATP molecule/products of its hydrolysis. A substantial shift of the electronic energy levels can then be induced [146]. In a simple setting, the corresponding modulation of an energy level can be modelled by a two-state Markovian process [147]. The chemical source of driving force can also be substituted by a direct application of a stochastic electric field [147, 148]. This latter possibility has been demonstrated experimentally for some ion pumps [148].

which is coupled to a bath of independent harmonic oscillators, possessing the spectrum $\{\omega_\lambda\}$, i.e.,

$$H_B = \sum_\lambda \hbar\omega_\lambda \left(b_\lambda^\dagger b_\lambda + \frac{1}{2} \right), \tag{66}$$

where $b_\lambda^\dagger$ and b_λ are the bosonic creation and annihilation operators, respectively. The interaction with the thermal bath causes the relaxation transitions between the eigenstates of the dynamical system (''longitudinal'' interaction). Such transitions are absent otherwise and thus require either the emission, or the absorption of bath phonons. The interaction is chosen to be of a bi-linear form, reading

$$V_{SB} = \hat{\xi}(|1\rangle\langle 2| + |2\rangle\langle 1|), \tag{67}$$

with the influence of the bath being presented by a *random force operator*, $\hat{\xi}_{12} = \hat{\xi}_{21}^\dagger = \hat{\xi}$,

$$\hat{\xi} = \sum_\lambda \kappa_\lambda \left(b_\lambda^\dagger + b_\lambda \right). \tag{68}$$

Here and elsewhere below, the (real-valued) coupling constants κ's are included into the fluctuating force $\hat{\xi}$. From a phenomenological perspective, the considered model represents an analogue of the model in section 2.3.2, where a classical random force assuming two values is replaced by a quantum operator force which possesses a Gaussian statistics. Moreover, a possible time-dependence of the energy levels is assumed here.

The corresponding correlation function of this Gaussian quantum stochastic force $K(t) := K_{1221}(t) = \langle \hat{\xi}_{12}(t)\hat{\xi}_{12}^\dagger(0)\rangle$ is complex-valued. It reads explicitly

$$K(t) = \frac{1}{2\pi}\int_0^\infty J(\omega)\left[\coth\left(\frac{\hbar\omega}{2k_B T} \right)\cos(\omega t) - i\sin(\omega t) \right] d\omega, \tag{69}$$

with the bath spectral density given by

$$J(\omega) := \frac{2\pi}{\hbar^2}\sum_\lambda \kappa_\lambda^2 \delta(\omega - \omega_\lambda). \tag{70}$$

Upon extending to negative frequencies $\omega < 0$, it is convenient to formally define $J(-\omega) := -J(\omega)$.

The complex nature of this bath correlation function is crucial for the establishment of thermal equilibrium at the finite temperatures. The application of GME (61), (62) to the present case yields a closed system of GMEs for the level populations $p_n(t) := \rho_{nn}(t), n = 1, 2$, reading,

$$\begin{aligned} \dot{p}_1(t) &= -\int_0^t [w_{12}(t,t')p_1(t') - w_{21}(t,t')p_2(t')]dt', \\ \dot{p}_2(t) &= \int_0^t [w_{12}(t,t')p_1(t') - w_{21}(t,t')p_2(t')]dt', \end{aligned} \tag{71}$$

with memory kernels[13]

$$w_{12}(t,t') = 2\mathrm{Re}[K(t-t')\exp(i\epsilon_0(t-t') + i\tilde{\zeta}(t,t')],$$
$$w_{21}(t,t') = 2\mathrm{Re}[K(t-t')\exp(-i\epsilon_0(t-t') - i\tilde{\zeta}(t,t')], \tag{72}$$

where $\epsilon_0 = (E_1^{(0)} - E_2^{(0)})/\hbar$ and $\tilde{\zeta}(t,t')$ is a functional of time-dependent driving, equation (46), with $\tilde{\epsilon}(t) = [\tilde{E}_1(t) - \tilde{E}_2(t)]/\hbar$. We shall assume that $\tilde{\epsilon}(t)$ fluctuates (either randomly, or periodically in time) around a zero mean value. In order to obtain the quantum relaxation averaged over the fluctuations of $\tilde{\epsilon}(t)$ one needs to perform a corresponding stochastic averaging of the GME (71). For an arbitrary stochastic process $\tilde{\epsilon}(t)$, this task cannot be carried out exactly any longer; consequently one must resort to some approximation scheme(s).

5.1. *Decoupling approximation for fast fluctuating energy levels*

If the characteristic time-scale for $\tilde{\epsilon}(t)$ fluctuations τ_ϵ is very small in comparison with the characteristic system relaxation time-scale τ_r, i.e. $\tau_\epsilon \ll \tau_r$, then one can use a decoupling approximation by averaging for $\langle p_{1,2}(t)\rangle_\epsilon$; namely, $\langle \exp(\pm i\tilde{\zeta}(t,t')p_{1,2}(t')\rangle_\epsilon \approx \langle \exp(\pm i\tilde{\zeta}(t,t')\rangle_\epsilon \langle p_{1,2}(t')\rangle_\epsilon$. For fast fluctuations of the energy levels the relaxation dynamics then follows $\langle p_{1,2}(t)\rangle_\epsilon$ with fast, superimposed small-amplitude fluctuations whose amplitude diminishes when the ratio $\tau_\epsilon/\tau_r \ll 1$ becomes smaller. A subsequent Markovian approximation for the averaged dynamics yields a master equation description of the form:

$$\langle \dot{p}_1(t)\rangle_\epsilon = -\langle W_{12}(\epsilon_0)\rangle_\epsilon \langle p_1(t)\rangle_\epsilon + \langle W_{21}(\epsilon_0)\rangle_\epsilon \langle p_2(t)\rangle_\epsilon,$$
$$\langle \dot{p}_2(t)\rangle_\epsilon = \langle W_{12}(\epsilon_0)\rangle_\epsilon \langle p_1(t)\rangle_\epsilon - \langle W_{21}(\epsilon_0)\rangle_\epsilon \langle p_2(t)\rangle_\epsilon \tag{73}$$

with the averaged transition rates reading [64],

$$\langle W_{12}(\epsilon_0)\rangle_\epsilon = \int_{-\infty}^{\infty} e^{\hbar\omega/k_BT} n(\omega) J(\omega) I(\epsilon_0 - \omega) d\omega,$$
$$\langle W_{21}(\epsilon_0)\rangle_\epsilon = \int_{-\infty}^{\infty} n(\omega) J(\omega) I(\epsilon_0 - \omega) d\omega\ . \tag{74}$$

Here $n(\omega) = 1/[\exp(\hbar\omega/(k_BT)) - 1]$ is the Bose function, and $I(\omega)$ is the spectral line shape of a Kubo oscillator $\dot{X}(t) = i\tilde{\epsilon}(t)X(t)$ (see in section 2). From equations (73), (74) one can immediately deduce that in the absence of fluctuations, where $I(\omega) = \delta(\omega)$, the thermal equilibrium, $p_1(\infty) = e^{-\hbar\epsilon_0/k_BT} p_2(\infty)$, is attained independently of the specific model for $J(\omega)$ for arbitrary temperatures T. Moreover, the thermal detailed balance condition, $p_2(\infty)W_{21}(\epsilon_0) = p_1(\infty)W_{12}(\epsilon_0)$ is obeyed always with the thermal bath temperature T. In other words, the temperature T_σ of the considered TLS, defined through equation (36) coincides with the temperature of the thermal bath T, $T_\sigma = T$. This is in a sharp contrast to the stochastic bath modelling in section 2.3.2, where we found that $p_1(\infty) = p_2(\infty)$ and $T_\sigma = \infty$. Furthermore, one can see that the thermal equilibrium at the bath temperature T becomes violated

[13]One can immediately see that if $K(t)$ would be real-valued, then the forward and backward rate kernels were always equal. This would mimic the situation of an infinite temperature as it was elucidated in section 2 for a classical stochastic bath.

either by periodic, or by stochastic nonequilibrium fluctuations. This also implies that, generally, $T_\sigma \neq T$. Put differently, either periodic, or stochastic (thermally nonequilibrium) fields drive the system *out of the thermal equilibrium* with the thermal bath. This fact lies at the heart for the emergence of a diversity of interesting and often counter-intuitive nonequilibrium effects which we shall address next.

5.1.1. Control of quantum rates. A first application is the manipulation of the transition rates by many orders of magnitude by use of a rapidly fluctuating, discrete stochastic fields [62, 64–66]. This scheme becomes feasible when the spectral density of the bath $J(\omega)$ is sharply peaked around some vibrational frequencies. The effect can be demonstrated for a quantum Brownian oscillator model of the bath: It corresponds to a single quantum vibrational mode Ω_0 which acquires a frictional broadening width γ due to a bi-linear coupling to other environmental vibrational modes.[14] The corresponding spectral density assumes the form [5]:

$$J(\omega) = \frac{8\kappa_0^2}{\hbar^2} \frac{\gamma\Omega_0\omega}{(\omega^2 - \Omega_0^2)^2 + 4\gamma^2\omega^2}. \tag{75}$$

Let us start out by considering first a control scenario of quantum relaxation by use of a symmetric dichotomous Markovian noise $\tilde{\epsilon}(t) = \pm\sigma$ with $I(\omega)$ given by (28), where $\epsilon_{1,2} = \pm\sigma$. For the case[15] $\nu \ll \sigma$, this spectral line shape consists of two sharply shaped peaks, located at $\omega = \pm\sigma$ and possessing the width ν. For $\nu \ll \gamma$, which is typically the case, this latter broadening can be neglected. Then, $I(\omega) \approx \frac{1}{2}[\delta(\omega - \sigma) + \delta(\omega + \sigma)]$, and the averaged rates simplify to read

$$\begin{aligned}\langle W_{12}(\epsilon_0)\rangle_\epsilon &\approx \frac{1}{2}[W_{12}(\epsilon_0 + \sigma) + W_{12}(\epsilon_0 - \sigma)] \\ &= \frac{4\kappa_0^2\gamma\Omega_0}{\hbar^2} \quad \frac{(\epsilon_0 - \sigma)e^{(\hbar(\epsilon_0 - \sigma)/k_BT)}n(\epsilon_0 - \sigma)}{[(\epsilon_0 - \sigma)^2 - \Omega_0^2]^2 + 4\gamma^2(\epsilon_0 - \sigma)^2} \\ &\quad + \frac{(\epsilon_0 + \sigma)e^{(\hbar(\epsilon_0 + \sigma)/k_BT)}n(\epsilon_0 + \sigma)}{[(\epsilon_0 + \sigma)^2 - \Omega_0^2]^2 + 4\gamma^2(\epsilon_0 + \sigma)^2}\Bigg)\end{aligned} \tag{76}$$

[14] A fast (on the time-scale τ_r of system relaxation) equilibration of this single mode with other vibrational modes is assumed. This imposes an important restriction $\tau_r^{-1} := \langle W_{12}(\epsilon_0)\rangle_\epsilon + \langle W_{21}(\epsilon_0)\rangle_\epsilon \ll \gamma$ which can always be justified by a proper tuning of the coupling constant κ_0. Furthermore, the broadening of vibrational spectral lines in molecular systems γ exceeds typically $\gamma > 5\,\mathrm{cm}^{-1}$ (in spectroscopic units) which corresponds $\gamma > 10^{12}$ Hz in units of the frequency. The considered relaxation transitions must consequently occur more slowly, e.g., an (ET) can occur on a msec time-scale [11].

[15] This case presents a realistic situation for experimental realisations of molecular systems since a significant stochastic perturbation with an energy exceeding one k_BT, $\hbar\sigma \sim 25$ meV (at room temperatures), corresponds in the units of frequency $\sigma \sim 4 \times 10^{13}$ 1/s. The frequency ν of large amplitude bistable conformational fluctuations of molecular groups is typically much smaller.

$$\langle W_{21}(\epsilon_0)\rangle_\epsilon \approx \frac{1}{2}[W_{21}(\epsilon_0+\sigma)+W_{21}(\epsilon_0-\sigma)]$$
$$= \frac{4\kappa_0^2\gamma\Omega_0}{\hbar^2}\left(\frac{(\epsilon_0-\sigma)n(\epsilon_0-\sigma)}{[(\epsilon_0-\sigma)^2-\Omega_0^2]^2+4\gamma^2(\epsilon_0-\sigma)^2}\right.$$
$$\left.+\frac{(\epsilon_0+\sigma)n(\epsilon_0+\sigma)}{[(\epsilon_0+\sigma)^2-\Omega_0^2]^2+4\gamma^2(\epsilon_0+\sigma)^2}\right).$$

From equation (76) it follows that if the quantum transition frequency ϵ_0 matches the vibrational frequency of the medium Ω_0 an increase of energy fluctuation size σ (induced by local electric field fluctuations in the medium) from zero to some finite value $\sigma \gg \gamma$ can drastically reduce the relaxation rate $\Gamma_0(\epsilon_0) = \langle W_{12}(\epsilon_0)\rangle_\epsilon + \langle W_{21}(\epsilon_0)\rangle_\epsilon$; even a practical blockade of relaxation transitions can occur [62, 64–66]. On the contrary, in the case of a frequency mismatch between ϵ_0 and Ω_0 one in turn can dramatically enhance the rate of relaxation transitions by tuning the noise amplitude σ appropriately [66], see in figure 4a.

5.1.2. Stochastic cooling and inversion of level populations. A second effect relates to the blockage of the rate for backward transitions $\langle W_{21}(\epsilon_0)\rangle_\epsilon$ relative to the forward rate $\langle W_{12}(\epsilon_0)\rangle_\epsilon$. This can cause a *stochastic cooling* of the TLS, where the temperature T_σ becomes *smaller* than the temperature of the environment, i.e., $T_\sigma < T$. This interesting phenomenon is demonstrated with figure 4b. Similar in spirit, although different in the physical mechanism is the laser cooling (of the nuclear degrees of freedom) as it has been studied both, theoretically and experimentally for polyatomic molecules [149].

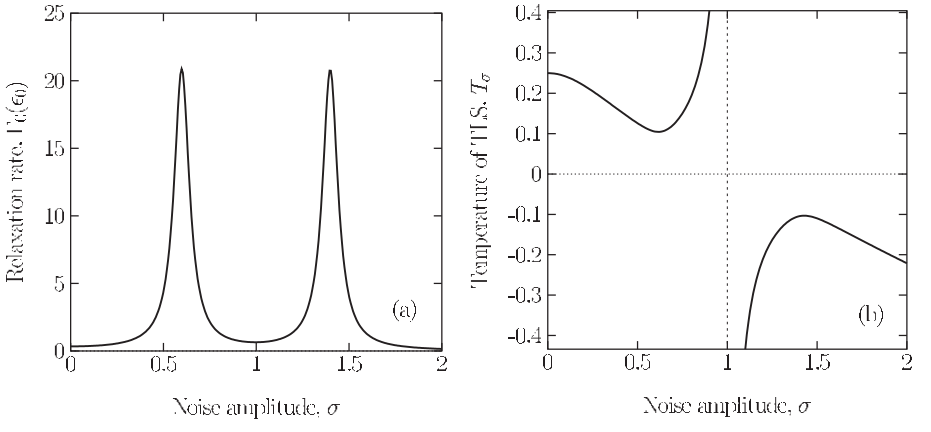

Figure 4. (a) The averaged relaxation rate of TLS, $\Gamma_0(\epsilon_0)$, in units of $\kappa_0^2/(\hbar^2\Omega_0)$, is depicted versus the noise amplitude σ (in units of Ω_0) for the averaged energy bias $\epsilon_0 = 0.4\Omega_0$ and the thermal bath temperature $T = 0.25\hbar\Omega_0/k_B$ and $\gamma = 0.05\Omega_0$. (b) The effective temperature of TLS, T_σ, in units of $\hbar\Omega_0/k_B$ versus the noise amplitude σ (in units of Ω_0) for the same set of parameters of TLS and the environmental temperature T. At $\sigma \approx 0.6\Omega_0$, where the TLS is maximally cooled, the lower level is populated with the probability being close to one. On the contrary, for $\sigma \approx 1.4\Omega_0$ the upper level becomes populated with the probability being close to one; i.e., an almost complete inversion of populations occurs. The model assumptions are well justified for the coupling constant $\kappa_0 \ll 0.05\hbar\Omega_0$ such that $\Gamma_0(\epsilon_0) \ll \gamma$.

Moreover, for $\sigma > \Omega_0$ a noise-induced inversion of steady state averaged populations takes place, i.e., for a sufficiently small positive energy bias ϵ_0 the higher energy level becomes more populated. This constitutes the third very important effect under discussion, see figure 4b, where this pumping effect is interpreted in terms of a *negative* temperature T_σ. In other words, the considered nonequilibrium noise of a sufficiently large amplitude is capable to pump quantum particles from the lower energy level to the higher one. This provides a possible archetype for quantum molecular pumps driven by nonequilibrium noise.

This inversion of population can be accompanied by cooling. Namely, the ensemble of TLSs becomes first effectively cooled and only then heated up (through, formally, $T_\sigma = \infty$ to $T_\sigma = -\infty$) until the inversion of population occurs – cf. in figure 4b. For this pumping mechanism to work, an *inverted transport regime* [184] is necessary; i.e., a regime where the static, unfluctuating forward rate becomes smaller with the increasing energy bias after reaching a maximum at ϵ_{max}. In the present model, this maximum is located in the neighbourhood of Ω_0. More precisely, ϵ_{max} corresponds to the maximum in the difference between the forward and the backward rates, rather than to the maximum of the forward rate alone. The inversion happens for $\sigma > \epsilon_{max}$ and a sufficiently small energy bias ϵ_0. A similar mechanism has been proposed in [68] within a spin-boson modelling of electron tunnelling in proteins, see below in section 6, driven by nonequilibrium conformational fluctuations, e.g., utilising energy of ATP hydrolysis.

The underlying mechanism seems quite general. Indeed, the inversion of populations occurs whenever the difference of averaged rates $\langle \Delta W(\epsilon_0)\rangle_\epsilon := \langle W_{12}(\epsilon_0)\rangle_\epsilon - \langle W_{21}(\epsilon_0)\rangle_\epsilon$ becomes negative, $\langle \Delta W(\epsilon_0)\rangle_\epsilon < 0$, for a positive bias $\epsilon_0 > 0$. In the discussed limiting case, $\langle \Delta W(\epsilon_0)\rangle_\epsilon \approx \frac{1}{2}[\Delta W(\epsilon_0 + \sigma) + \Delta W(\epsilon_0 - \sigma)]$ with $\Delta W(-\epsilon) = -\Delta W(\epsilon)$. Therefore, when σ exceeds ϵ_{max}, where $\Delta W(\epsilon)$ achieves a maximum and $\frac{d}{d\epsilon}\Delta W(\epsilon) < 0$ for $\sigma > \epsilon_{max}$, the averaged difference of forward and backward rates becomes negative $\langle \Delta W(\epsilon_0)\rangle_\epsilon < 0$, for a positive energy bias $\epsilon_0 > 0$, i.e. an inversion of populations takes place. In application to the quantum transport in a spatially extended system, a similar effect results in the noise-induced absolute negative mobility [69], see below in section 7. The existence of the static current-voltage characteristics with a negative *differential* conductivity part is important for the latter phenomenon to occur.

5.1.3. Emergence of an effective energy bias. The fourth important effect, the onset of which can be seen already in the discussed archetype model, is rooted in a possible asymmetry of the unbiased on average fluctuations. Namely, let us consider the symmetric quantum system, $\epsilon_0 = 0$, with asymmetric dichotomous fluctuations of the energy levels with zero mean, see in section 2.3.1. Since in this case, the averaged propagator of the corresponding Kubo oscillator is *complex-valued*, $\mathrm{Im}\,\langle \exp[i\tilde{\xi}(t, t')]\rangle_\epsilon \neq 0$, it can be readily seen from equation (72) after invoking the decoupling approximation that $\langle w_{12}(t, t')\rangle_\epsilon - \langle w_{21}(t, t')\rangle_\epsilon \neq 0$ even if $\epsilon_0 = 0$. This means that an effective asymmetry emerges. Moreover, the above difference is proportional also to $\mathrm{Im}\,K(t - t') \neq 0$. If the autocorrelation function of the thermal bath, $K(t)$, were real (like for a stochastic bath), then *no* asymmetry between the forward and backward rates could emerge in principle. Therefore, the discussed asymmetry does emerge due to a subtle interplay of the equilibrium

quantum fluctuations of the thermal bath and nonequilibrium classical fluctuations of the energy levels, both of which are unbiased on average. Here is rooted the origin of quantum dissipative rectifiers put forward in [70, 102]. The very same effect can also be deduced from equation (74), since the corresponding spectral line $I(\omega)$, cf. equation (28), is *asymmetric*. Yet, ultimate insight is achieved in the slow-modulation limit of the Kubo oscillator, $K_\epsilon := \sigma/\nu \gg 1$, like in equation (76) where the mean forward and backward rates are the static rates $W_{12}(\epsilon)$ and $W_{21}(\epsilon)$ averaged over the energy bias distribution, $p(\epsilon_{1,2}) = \langle\tau_{1,2}\rangle/(\langle\tau_1\rangle + \langle\tau_2\rangle)$, correspondingly, i.e., $\langle W_{12}(0)\rangle_\epsilon = \sum_{j=1,2} p(\epsilon_j) W_{12}(\epsilon_j)$ and $\langle W_{21}(0)\rangle_\epsilon = \sum_{j=1,2} p(\epsilon_j) W_{21}(\epsilon_j)$.

For several applications of quantum transport in spatially extended systems our driving-induced breaking of symmetry leads to a rectification current in tight-binding Brownian rectifiers [70, 102], see in section 7.

5.2. *Quantum relaxation in strong periodic fields*

The considered strong nonequilibrium effects are present as well in the case of a fast periodic driving, $\tilde{\epsilon}(t) = A\cos(\Omega t + \varphi_0)$, with a static phase φ_0 which is uniformly distributed between 0 and 2π. Then, the corresponding spectral line shape form $I(\omega)$ is $I(\omega) = \sum_{n=-\infty}^{\infty} J_n^2(A/\Omega)\delta(\omega - n\Omega)$, where $J_n(z)$ is the Bessel function of the first kind.

The rate expressions (76) take on the form

$$\langle W_{12}(\epsilon_0)\rangle_\epsilon = \sum_{n=-\infty}^{\infty} J_n^2\Big(\frac{A}{\Omega}\Big) e^{\hbar[\epsilon_0 - n\Omega]/k_B T} n(\epsilon_0 - n\Omega) J(\epsilon_0 - n\Omega),$$

$$\langle W_{21}(\epsilon_0)\rangle_\epsilon = \sum_{n=-\infty}^{\infty} J_n^2\Big(\frac{A}{\Omega}\Big) n(\epsilon_0 - n\Omega) J(\epsilon_0 - n\Omega). \tag{77}$$

Such an expansion of the transition rates as a sum over different emission (absorption) channels with n emitted (absorbed) photons with the corresponding probabilities $p_n = J_n^2(A/\Omega)$ is similar to one used by Tien and Gordon in a different context [3, 150]. For the averaged relaxation rate the above expression yields the same result as in [82] where the principal possibility to regulate quantum relaxation processes in condensed molecular systems by strong periodic external fields has been indicated. Moreover, the inversion of populations by periodic driving takes also place for the above model $J(\omega)$ and some properly adjusted parameters of the periodic driving. For a periodically driven spin-boson model (see below in section 6) and a strong system-bath coupling, this latter effect has been theoretically predicted and described in [83, 89] (see also [3] for a review and further references). For the case of a weak system-bath coupling, the inversion of populations in the spin-boson model has been shown in [87].

5.3. *Approximation of time-dependent rates*

If the external field varies sufficiently slow on the characteristic time-scale, τ_d, describing the decay of the kernels in equation (71), an adiabatic approximation of time-dependent rates that follow the time-variation of the energy levels

can be invoked; i.e.,

$$\dot{p}_1(t) = -W_{12}(\epsilon(t))p_1(t) + W_{21}(\epsilon(t))p_2(t),$$
$$\dot{p}_2(t) = W_{12}(\epsilon(t))p_1(t) - W_{21}(\epsilon(t))p_2(t), \tag{78}$$

where $W_{21}(\epsilon) = n(\epsilon)J(\epsilon)$ and $W_{12}(\epsilon) = \exp(\hbar\epsilon/k_BT)W_{21}(\epsilon)$ are the static rates. For discrete state noise, this approximation holds whenever $\langle\tau_j\rangle \gg \tau_d$. Then, the corresponding rates describe a discrete state stochastic process and the averaging method of section 2 can be applied. In this limiting case, the corresponding Laplace-transformed averaged populations can be given in exact analytical form. In the considered case this corresponds to the averaging of a Kubo oscillator with an imaginary frequency. The corresponding averaged solution can be analytically inverted into the time domain in the case of two-state Markovian fluctuations. This solution is generally bi-exponential. Two limiting cases can be distinguished which can be classified by the Kubo number K_W of the *rate* fluctuations, i.e. by the product of the variance of the rate fluctuations multiplied with the corresponding autocorrelation time. In a *slow modulation* limit (in terms of the *rate* fluctuations), $K_W \gg 1$ and the (ensemble) averaged relaxation is approximately described by a quasi-static averaging of the time-dependent solutions with the static, "frozen" energy bias randomly distributed. It assumes a bi-exponential form, but can be multi-exponential and anomalously slow in a more general case of multi-state fluctuations. The opposite limit of *fast modulation* (in terms of the *rate* fluctuations, $K_W \ll 1$) corresponds to the averaged rate description which is detailed above and which invokes the decoupling approximation and in addition can possibly involve a *slow modulation* limit in terms of the *energy* level fluctuations, $K_\epsilon \gg 1$. The resulting averaged relaxation process remains approximately single-exponential.

In view of the presence of many different time-scales the underlying physics is nontrivial. Therefore, it is useful to be able to resort to a case study where the stochastic averaging can be performed *exactly*. Such an archetypal investigation has been put forward in [100] and has been applied to the stochastic spin-boson model in [68, 101].

5.4. *Exact averaging for dichotomous Markovian fluctuations*

By use of the conservation of probabilities, the system of integro-differential equations (71) can be reduced to a single equation for the *difference of populations* $\sigma_z(t) = p_1(t) - p_2(t)$. It reads:

$$\dot{\sigma}_z(t) = -\int_0^t f(t,t')\sigma_z(t')dt' - \int_0^t g(t,t')dt' \tag{79}$$

with the integral kernels

$$f(t,t') = f_0(t,t')\cos[\epsilon_0(t-t') + \tilde{\xi}(t,t')],$$
$$g(t,t') = g_0(t,t')\sin[\epsilon_0(t-t') + \tilde{\xi}(t,t')], \tag{80}$$

where

$$f_0(t,t') = f_0(t-t') = 4\ \mathrm{Re}[K(t-t')],$$
$$g_0(t,t') = g_0(t-t') = -4\ \mathrm{Im}[K(t-t')]. \tag{81}$$

The kernel $f(t,t')$ in equation (79) denotes a stochastic functional of the driving field $\tilde{\epsilon}(t)$ on the time interval $[t',t]$ (with times later than t') whereas $\sigma_z(t')$ is a functional of the dichotomous Markovian process (DMP) for the times prior to t'. The task of stochastic averaging of the product of such functionals, $\langle f(t,t')\sigma_z(t')\rangle$, can become very difficult, see [151]. However, in the case $\tilde{\epsilon}(t)=\sigma\alpha(t)$, where $\alpha(t)=\pm 1$ is symmetric DMP with unit variance and an autocorrelation time $\tau_c=1/\nu$ this task can be solved exactly by referring to a theorem by Bourret, Frisch and Pouquet [152] (for a different proof of this remarkable exact result, see also [153]). It reads: $\langle f(t,t'+\tau)\alpha(t'+\tau)\alpha(t')\sigma_z(t')\rangle = \langle f(t,t'+\tau)\rangle\langle\alpha(t'+\tau)\alpha(t')\rangle\langle\sigma_z(t')\rangle + \langle f(t,t'+\tau)\alpha(t'+\tau)\rangle\times\langle\alpha(t')\sigma_z(t')\rangle$ for $\tau\geq 0$. By passing to the limit $\tau\to 0$ and using the characteristic property of the DMP, namely that $\alpha^2(t)=1$ (without averaging), the above relation yields an important corollary [100]:

$$\langle f(t,t')\sigma_z(t')\rangle = \langle f(t,t')\rangle\langle\sigma_z(t')\rangle + \langle f(t,t')\alpha(t')\rangle\langle\alpha(t')\sigma_z(t')\rangle. \tag{82}$$

This result is beyond the decoupling approximation, given by the first term in the sum. The result for the cross-correlation function $\langle\alpha(t)\sigma_z(t)\rangle$ is more intricate. The equation of motion for this cross-correlation function can be obtained thanks to a theorem by Shapiro-Loginov [51, 154], reading,

$$\frac{d}{dt}\langle\alpha(t)\sigma_z(t)\rangle = -\nu\langle\alpha(t)\sigma_z(t)\rangle + \left\langle\alpha(t)\frac{d\sigma_z(t)}{dt}\right\rangle. \tag{83}$$

Use of this relation in turn generates an integro-differential equation for $\langle\alpha(t)\sigma_z(t)\rangle$, where the problem of decoupling of $\langle\alpha(t)f(t,t')\sigma_z(t')\rangle$ emerges. It can be solved in the same way as in equation (82), namely

$$\langle\alpha(t)f(t,t')\sigma_z(t')\rangle = \langle\alpha(t)f(t,t')\rangle\langle\sigma_z(t')\rangle + \langle\alpha(t)f(t,t')\alpha(t')\rangle\langle\alpha(t')\sigma_z(t')\rangle. \tag{84}$$

All these averaged functionals, like $\langle f(t,t')\rangle$, $\langle\alpha(t)f(t,t')\rangle$, $\langle f(t,t')\alpha(t')\rangle$, $\langle\alpha(t)f(t,t')\alpha(t')\rangle$ can be expressed in terms of the averaged propagator of the corresponding Kubo oscillator $S^{(0)}(t-t')=\langle\exp[i\sigma\int_{t'}^{t}\alpha(\tau)d\tau]\rangle$ given in equation (29) with $\chi=\nu/2$ (zero asymmetry), and its derivatives $S^{(n)}(t):=(1/\sigma^n)(d^n/dt^n)S^{(0)}(t)$ [100, 101]. Applying the general results in equations (82), (83) and (84) to equation (79) yields a closed system of two integro-differential equations [100, 101]:

$$\begin{aligned}\frac{d}{dt}\langle\sigma_z(t)\rangle = -\int_0^t\Big(&S^{(0)}(t-t')f_0(t-t')\cos[\epsilon_0(t-t')]\langle\sigma_z(t')\rangle\\ &- S^{(1)}(t-t')f_0(t-t')\sin[\epsilon_0(t-t')]\langle\alpha(t')\sigma_z(t')\rangle\\ &+ S^{(0)}(t-t')g_0(t-t')\sin[\epsilon_0(t-t')]\Big)dt',\end{aligned} \tag{85}$$

$$\begin{aligned}\frac{d}{dt}\langle\alpha(t)\sigma_z(t)\rangle = -\nu\langle\alpha(t)\sigma_z(t)\rangle + \int_0^t\Big(&S^{(2)}(t-t')f_0(t-t')\cos[\epsilon_0(t-t')]\langle\alpha(t')\sigma_z(t')\rangle\\ &+ S^{(1)}(t-t')f_0(t-t')\sin[\epsilon_0(t-t')]\langle\sigma_z(t')\rangle\\ &+ S^{(1)}(t-t')g_0(t-t')\cos[\epsilon_0(t-t')]\Big)dt'.\end{aligned}$$

A subsequent Markovian approximation for equation (85) then yields [100]:

$$\frac{d}{dt}\langle\sigma_z(t)\rangle = -\Gamma_0\langle\sigma_z(t)\rangle - \Gamma_1\langle\alpha(t)\sigma_z(t)\rangle - r_0,$$
$$\frac{d}{dt}\langle\alpha(t)\sigma_z(t)\rangle = -\Gamma_1\langle\sigma_z(t)\rangle - (\nu+\Gamma_2)\langle\alpha(t)\sigma_z(t)\rangle - r_1 \tag{86}$$

with

$$\Gamma_k = \int_{-\infty}^{\infty} \coth\left(\frac{\hbar\omega}{2k_BT}\right) J(\omega) I_k(\epsilon_0-\omega)d\omega,$$
$$r_k = \int_{-\infty}^{\infty} J(\omega) I_k(\epsilon_0-\omega)d\omega, \tag{87}$$

where $I_k(\omega) = (-\omega/\sigma)^k I(\omega)$ and $I(\omega)$ is given in equation (28) with $\epsilon_{1,2} = \pm\sigma$. It can be shown that all known limiting cases are reproduced from this remarkable result.

For the case of weakly coloured noise $K_\epsilon \ll 1$ (i.e. the fast modulation limit of the Kubo oscillator), the spectral line $I(\omega)$ becomes a Lorentzian with the width $D = \sigma^2/\nu$. The same result holds true in the white noise limit $\sigma\to\infty, \nu\to\infty$, with $D = const$ and $K_\epsilon \to 0$. In these limits Γ_1 is negligible small, $\Gamma_1 \approx 0$, and the relaxation is described by the averaged rate Γ_0. Precisely the same result re-emerges also for white Gaussian noise $\tilde{\epsilon}(t)$ with the noise intensity D. The spectral line $I(\omega)$ becomes narrower when ν increases, – this constitutes the celebrated motional narrowing limit of NMR [33, 32] –, and approaches zero when $\nu\to\infty$ (with σ kept constant). Such infinitely fast fluctuations have no influence on the considered rate process; the field-free description is thus reproduced with the thermal equilibrium being restored.

In the slow modulation limit of the Kubo oscillator ($K_\epsilon \gg 1$), $I(\omega) \approx I_2(\omega) \approx \frac{1}{2}[\delta(\omega+\sigma)+\delta(\omega-\sigma)]$ and $I_1(\omega) \approx \frac{1}{2}[\delta(\omega+\sigma)-\delta(\omega-\sigma)]$, with the corresponding line widths neglected. In this case, the approximation of time-dependent fluctuating rates following adiabatically to the energy levels fluctuations becomes justified. The relaxation is generally bi-exponential with the two rates given by

$$\lambda_{1,2} = \frac{\nu}{2} + \Gamma_0 \pm \frac{1}{2}\sqrt{(\Gamma_+-\Gamma_-)^2+\nu^2}. \tag{88}$$

Here, $\Gamma_\pm = \coth[\hbar(\epsilon_0\pm\sigma)/2k_BT]J(\epsilon_0\pm\sigma)$ is the relaxation rate in the quasi-static limit and $\Gamma_0 = (\Gamma_+ + \Gamma_-)/2$. Furthermore, if $\nu \gg \Gamma_0$, we have $\lambda_1 \approx \nu$ (note that the corresponding exponent $\exp(-\lambda_1 t)$ contributes, however, with a very small weight), and $\lambda_2 \approx \Gamma_0$ (with a weight which approximately equals one): This in turn implies that the relaxation is practically single exponential with rate Γ_0 and corresponds to the fast modulation limit in terms of the fluctuating rates.

6. Application II: Driven electron transfer within a spin-boson description

Let us proceed with an application of our general theory to the celebrated *driven* spin-boson model [3]. This model is of special importance since it describes a large variety of physical phenomena [1, 2], such as relevant aspects of ET in molecular systems.

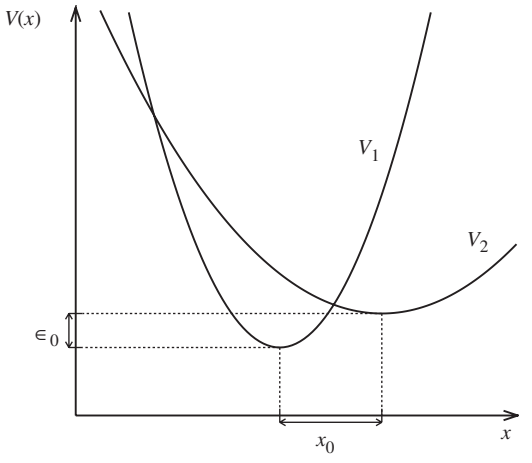

Figure 5. Sketch of the diabatic electronic curves. Note that two crossing points occur in the presence of different curvatures [160].

6.1. *Curve-crossing problems with dissipation*

The simplest case of a two-state donor–acceptor ET reaction can be considered as a curve-crossing problem within the description of two diabatic electronic states $|1\rangle$ and $|2\rangle$ with electronic energies $V_1(x)$ and $V_2(x)$ that depend on a nuclear reaction coordinate x [8, 9, 157–159] (cf. figure 5). Namely, after separating nuclear and electronic degrees of freedom within the Born-Oppenheimer approximation, the electron tunnelling process coupled to the nuclear dynamics (modelled by the reaction coordinate x) can be described by the following Hamiltonian

$$H_{tun}(x,p,t) = \left[\frac{\hat{p}^2}{2M} + V_1(x,t)\right]|1\rangle\langle 1| + \left[\frac{\hat{p}^2}{2M} + V_2(x,t)\right]|2\rangle\langle 2| + \frac{1}{2}\hbar\Delta(t)\big(|1\rangle\langle 2| + |2\rangle\langle 1|\big). \tag{89}$$

The time-dependent electronic curves in equation (89)

$$V_{1,2}(x,t) = \frac{1}{2}M\Omega_{1,2}^2(x \pm x_0/2)^2 \pm \hbar\epsilon_0/2 - d_{1,2}\mathcal{E}(t), \tag{90}$$

can generally possess different curvatures in the parabolic approximation with minima energetically separated by $\hbar\epsilon_0$ and separated by a distance x_0 (the tunnelling distance). Moreover, such electronic states generally possess electric dipole moments $d_{1,2}$ (their coordinate dependence is neglected) and thus the discussed energy levels will generally become dependent either on the stochastic microscopic fields of the environment, or on an externally applied electric field $\mathcal{E}(t)$. The corresponding time-dependence can likewise reflect also some nonequilibrium conformational dynamics. Moreover, the coupling or tunnelling matrix element $\Delta(t)$ can also parametrically depend on a nonequilibrium reaction coordinate which generally introduces an explicit stochastic time-dependence. The reaction coordinate x is coupled to the

rest of vibrational degrees of freedom of the environment. This introduces a dissipation mechanism into the tunnelling problem which can be modelled by a bilinear coupling of x to the thermal bath of harmonic oscillators [5, 20],

$$H_{\mathrm{BI}} = \frac{1}{2}\sum_i \left\{ \frac{\hat{p}_i^2}{m_i} + m_i\omega_i^2\left[x_i - \frac{c_i}{m_i\omega_i^2}x\right]^2\right\}. \tag{91}$$

It is worth pointing out that the frequencies $\Omega_{1,2}$ of the oscillator x can depend on the electronic state. In other words, the relevant vibration modes can become either softer, or more rigid depending on the electronic state. In the following, we neglect this possible effect and assume that $\Omega_1 = \Omega_2 = \Omega_0$, but note the studies in [155, 156, 160] for the more general situation. Moreover, one assumes that the reaction coordinate relaxes rapidly (with respect to the time-scale of ET) into thermal equilibrium with the bath of oscillators. Then, a canonical transformation from the "reaction coordinate + N bath oscillators" to "N + 1 new bath oscillators" brings the original problem into the spin-boson form, i.e., [5]

$$H(t) = \frac{1}{2}\hbar\epsilon(t)\hat{\sigma}_z + \frac{1}{2}\hbar\Delta(t)\hat{\sigma}_x + \frac{1}{2}x_0\hat{\sigma}_z\sum_\lambda \tilde{c}_\lambda\tilde{x}_\lambda + \frac{1}{2}\sum_\lambda\left\{\frac{\tilde{p}_\lambda^2}{\tilde{m}_\lambda} + \tilde{m}_\lambda\tilde{\omega}_\lambda^2\tilde{x}_\lambda^2\right\}, \tag{92}$$

where $\epsilon(t) = \epsilon_0 - (d_1 - d_2)\mathcal{E}(t)/\hbar$. The coupling between the quasi-spin and boson bath is characterised by a so-called spectral density[16] $\tilde{J}(\omega) = (\pi/2)\sum_i(\tilde{c}_\lambda^2/\tilde{m}_\lambda\tilde{\omega}_\lambda)\times\delta(\omega - \tilde{\omega}_\lambda)$ [1]. Moreover, we assume for the low frequency behaviour an Ohmic-like coupling between the reaction coordinate and the environmental vibrational modes (which corresponds in the classical limit to a viscous frictional force $F = -\zeta\dot{x}$ acting on the reaction coordinate x) which in turn yields the effective spectral density $\tilde{J}(\omega) = \zeta\omega(\Omega_0^4/((\omega^2 - \Omega_0^2)^2 + 4\omega^2\gamma^2))$; $\gamma = \zeta/2M$. This scheme corresponds to the model of a damped Brownian harmonic oscillator used in equation (75) with $\kappa_0 = \sqrt{(\hbar\Omega_0)\lambda}$, where $\lambda = Mx_0^2\Omega_0^2/2$ is the reorganisation energy. The coupling strength ζ can be related to the dimensionless (Kondo) parameter $\alpha = \zeta x_0^2/2\pi\hbar = (2/\pi)(\lambda/\hbar\Omega_0)(\gamma/\Omega_0)$. The use of the representation of bosonic operators in equation (6.1) then yields

$$H(t) = \frac{1}{2}\hbar\epsilon(t)\hat{\sigma}_z + \frac{1}{2}\hbar\Delta(t)\hat{\sigma}_x + \frac{1}{2}\hat{\sigma}_z\eta(t)\sum_\lambda\kappa_\lambda\left(b_\lambda^\dagger + b_\lambda\right) + \sum_\lambda\hbar\omega_\lambda\left(b_\lambda^\dagger b_\lambda + \frac{1}{2}\right) \tag{93}$$

(the "tilde" over ω_λ is omitted here). To address formally the most general case we assume in addition that the system-bath coupling can be modulated in time as well, i.e., $\kappa_\lambda \to \kappa_\lambda\eta(t)$ with some prescribed time-dependent function $\eta(t)$.

6.2. *Weak system-bath coupling*

Let us consider first the case of a weak system-bath coupling. The corresponding generalised master equations are obtained by applying equations (61), (62) (in the representation of $\hat{\gamma}_{nm}$) to the considered spin-boson model. This yields after some

[16]This definition is related to the one given in equation (70) by: $J(\omega) = 2x_0^2\tilde{J}(\omega)/\hbar$ with $\kappa_\lambda = x_0\tilde{c}_\lambda\sqrt{\hbar/(2\tilde{m}_\lambda\tilde{\omega}_\lambda)}$, $\tilde{x}_\lambda = \sqrt{\hbar/(2\tilde{m}_\lambda\tilde{\omega}_\lambda)}(b_\lambda^\dagger + b_\lambda)$.

cumbersome calculations by using the quasi-spin basis the following GMEs:

$$\dot{\sigma}_x(t) = -\epsilon(t)\sigma_y(t) - \int_0^t \Gamma_{xx}(t,t')\sigma_x(t')dt' - \int_0^t \Gamma_{xy}(t,t')\sigma_y(t')dt' - A_x(t),$$
$$\dot{\sigma}_y(t) = \epsilon(t)\sigma_x(t) - \Delta(t)\sigma_z(t) - \int_0^t \Gamma_{yx}(t,t')\sigma_x(t')dt' - \int_0^t \Gamma_{yy}(t,t')\sigma_y(t')dt' - A_y(t), \quad (94)$$
$$\dot{\sigma}_z(t) = \Delta(t)\sigma_y(t),$$

with the kernels reading

$$\Gamma_{xx}(t,t') = \eta(t)\eta(t')\mathrm{Re}[K(t-t')]\mathrm{Re}[U_{11}^2(t,t') + U_{12}^2(t,t')],$$
$$\Gamma_{yy}(t,t') = \eta(t)\eta(t')\mathrm{Re}[K(t-t')]\mathrm{Re}[U_{11}^2(t,t') - U_{12}^2(t,t')],$$
$$\Gamma_{xy}(t,t') = \eta(t)\eta(t')\mathrm{Re}[K(t-t')]\mathrm{Im}[U_{11}^2(t,t') - U_{12}^2(t,t')],$$
$$\Gamma_{yx}(t,t') = -\eta(t)\eta(t')\mathrm{Re}[K(t-t')]\mathrm{Im}[U_{11}^2(t,t') + U_{12}^2(t,t')], \quad (95)$$

and the inhomogeneous terms given by

$$A_x(t) = 2\int_0^t \eta(t)\eta(t')\mathrm{Im}[K(t-t')]\mathrm{Im}[U_{11}(t,t')U_{12}(t,t')]dt',$$
$$A_y(t) = 2\int_0^t \eta(t)\eta(t')\mathrm{Im}[K(t-t')]\mathrm{Re}[U_{11}(t,t')U_{12}(t,t')]dt' . \quad (96)$$

The evolution operator of the driven TLS in the absence of coupling, which defines the Hamiltonian $H_D(t)$ of the driven, nondissipative dynamics, is denoted by

$$U_{nm}(t,t') = \langle n|\mathcal{T}\exp\left[-\frac{i}{\hbar}\int_{t'}^t H_D(\tau)d\tau\right]|m\rangle.$$

This propagator enters the above memory kernels; it can be found numerically from the solution of the corresponding Schrödinger equation for an arbitrary time-dependence. Moreover, in the case of a periodic driving, an expansion into Floquet modes is conveniently applied, see in [161], and further references therein. Other methods, e.g., the use of a Magnus expansion [162] are also possible. Due to the unitary quantum evolution in the absence of dissipation we have $U_{22}(t,t') = U_{11}^*(t,t')$ and $U_{21}(t,t') = -U_{12}^*(t,t')$ with $\det[U_{nm}(t,t')] = 1$ for arbitrary time dependence of $\epsilon(t)$.

Time nonlocality of the GMEs in equation (94) makes them difficult to study from a numerical viewpoint. To work with a memoryless Markovian description presents, therefore, a pivotal advantage. If the dissipation is very weak, this description suffices to capture the main influences of dissipation on the driven quantum dynamics, i.e., the emergence of an exponential relaxation (and decoherence) described by some small rate constants and corresponding dissipation-induced frequency shifts, i.e. the Lamb shifts occurring even at $T = 0$. Both the relaxation rates and the frequency shifts are proportional, in the lowest order, to κ_λ^2. Applying equations (63), (64) to the considered dynamics yields the following driven Bloch-Redfield equations:

$$\dot{\sigma}_x(t) = -\epsilon(t)\sigma_y(t) - R_{xx}(t)\sigma_x(t) - R_{xz}(t)\sigma_z(t) - A_x(t),$$
$$\dot{\sigma}_y(t) = \epsilon(t)\sigma_x(t) - \Delta(t)\sigma_z(t) - R_{yy}(t)\sigma_y(t) - R_{yz}(t)\sigma_z(t) - A_y(t), \quad (97)$$
$$\dot{\sigma}_z(t) = \Delta(t)\sigma_y(t)$$

with the relaxation matrix elements reading

$$
\begin{aligned}
R_{xx}(t) = R_{yy}(t) &= \int_0^t \eta(t)\eta(t')\mathrm{Re}[K(t-t')][|U_{11}(t,t')|^2 - |U_{12}(t,t')|^2]dt', \\
R_{xz}(t) &= 2\int_0^t \eta(t)\eta(t')\mathrm{Re}[K(t-t')]\mathrm{Re}[\mathrm{U}_{11}(\mathrm{t},\mathrm{t}')\mathrm{U}_{12}(\mathrm{t},\mathrm{t}')]dt', \\
R_{yz}(t) &= -2\int_0^t \eta(t)\eta(t')\mathrm{Re}[K(t-t')]\mathrm{Im}[\mathrm{U}_{11}(\mathrm{t},\mathrm{t}')\mathrm{U}_{12}(\mathrm{t},\mathrm{t}')]dt'.
\end{aligned}
\tag{98}
$$

In the common case of a time-independent tunnelling matrix element, i.e. $\Delta(t) = const$ and a time-independent system-bath coupling, i.e. $\eta(t) = 1$ (what is assumed in the following), this result reduces to the driven Bloch-Redfield equations derived in [87]. Note the different signs of Δ and ϵ used throughout this work and in [87], as well as some other cited references.

For constant bias $\epsilon(t) = \epsilon_0$, and constant tunnelling coupling $\Delta(t) = \Delta$,

$$
\begin{aligned}
U_{11}(t,t') &= \cos[\omega_0(t-t')/2] - i\frac{\epsilon_0}{\omega_0}\sin[\omega_0(t-t')/2], \\
U_{12}(t,t') &= -i\frac{\Delta}{\omega_0}\sin[\omega_0(t-t')/2],
\end{aligned}
\tag{99}
$$

where $\omega_0 = \sqrt{\epsilon_0^2 + \Delta^2}$. Then, the equations reduce to the non-driven Bloch-Redfield equations of [163]. Some different weak-coupling master equations for the driven spin-boson model have been derived in [94] using the path integral approach. The equation for $\sigma_z(t)$ (not shown here) has the form of a *closed* integro-differential equation of rather involved form. In the limit of vanishing dissipation it reduces to equation (45) derived within a projection operator formalism.

The *numerical* equivalence of the our driven Bloch-Redfield equations and the weak-coupling integro-differential equation of [94] has been demonstrated in [87], both by comparison of the numerical solutions of both equations for the initial-to-intermediate part of the relaxation time-scale and by comparison of the numerical solution of the Bloch-Redfield equation and an approximate analytical solution of the weak-coupling GME of path-integral approach on the *whole* relaxation time-scale. This numerical comparison has been performed for periodically driven case, $\epsilon(t) = -\epsilon_0 - s\cos(\Omega t)$, for the Ohmic bath with exponential cutoff, $J(\omega) = 4\pi\alpha\omega e^{-\omega/\omega_c}$, where α is the dimensionless coupling strength (Kondo parameter) which has to be sufficiently small.[17]

Both approaches agree quite well, cf. in figure 6. The presented approach, however, is technically more convenient. The results possess a broad range of applications; for example, it allows one to study a mechanism of suppression of quantum

[17] An important restriction is: $\alpha(\Delta/\omega_0)^2\ln(\omega_c/\omega_0) \ll 1$ for $\omega_c \gg \omega_0$. It stems from the requirement of the smallness of the frequency Lamb shift, $\omega_0 \to \omega_r$, at $T = 0$. This restriction is most crucial for $\epsilon_0 = 0$, where $\omega_0 = \Delta$ and $\omega_r = \Delta_r \approx \Delta[1 - \alpha\ln(\tilde{\omega}_c/\Delta)] \approx \Delta\exp[-\alpha\ln(\tilde{\omega}_c/\Delta)] \approx \Delta(\Delta/\tilde{\omega}_c)^{\alpha/(1-\alpha)}$ (for $\alpha \ll 1$, to the linear order in $\alpha\ln(\tilde{\omega}_c/\Delta)$). Thus, this frequency shift is consistent with the renormalisation in section 6.3. For a large asymmetry $\epsilon_0 \gg \Delta$, the validity range of Bloch-Redfield equations in α becomes broader.

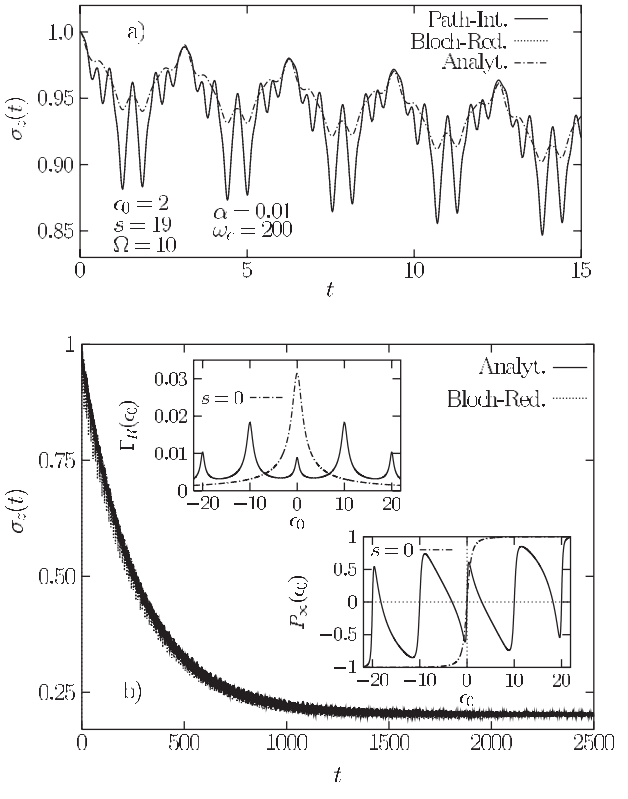

Figure 6. (a) Numerical comparison of the driven Bloch-Redfield equations of [87] (dotted line) and the path-integral GME of [94] (full line) for an oscillatory high-frequency driving $\Omega \gg \omega_0$ (data taken from [87]). Both depicted numerical solutions practically coincide within line width. The dashed-dotted line depicts a quasi-analytical solution (for details see in [87]) of the driven path-integral GME. It captures well the main features of the driven dynamics, lacking only some finer details. Time and frequencies are measured in units of Δ^{-1} and Δ, correspondingly. The used parameter sets are depicted in the figure. (b) Corresponding asymptotic long-time dynamics: the numerical solution of the driven Bloch-Redfield equations (dotted line) is compared with the quasi-analytical solution of driven path-integral GME (full line). Both solutions agree well within the width of the small-amplitude, driving induced oscillations. The two insets depict the analytical results for the rate of averaged relaxation $\Gamma_R(\epsilon_0)$ and the difference of asymptotic populations $P_\infty(\epsilon_0) := -\lim_{t\to\infty} \sigma_z(t)$, respectively. The rate of incoherent relaxation Γ_R exhibits characteristic resonance peaks, being located at multiple integers of the driving frequency Ω. These peaks are shifted replicas of the dc-driven rate with different weights, i.e. the case with no oscillatory forcing acting (i.e. a vanishing driving amplitude $s = 0$). Thus, a suitable chosen static field ϵ_0 can enhance or suppress the decay of populations. The asymptotic population difference P_∞ exhibits a non-monotonic dependence versus the asymmetry ϵ_0 when combined with a high-frequency driving field. For appropriate values of bias ϵ_0, a population inversion takes place ($P_\infty < 0$ when $\epsilon_0 > 0$, and *vice versa*).

decoherence by strong periodic fields for a two-level atom dynamics in an optical cavity [164]. The investigation of similar mechanisms is also of prime importance for the investigation of the quantum decoherence in various quantum information processing applications [165].

6.3. *Beyond weak-coupling theory: Strong system-bath coupling*

Thus far we concentrated on the case of weak-coupling to quantum thermal heat bath, or the regime of weak dissipation, respectively. The analytic theory is, however, not restricted to the case of weak dissipation only. In fact, by use of a combination with the method of canonical (unitary) transformations one can study the opposite limit of strong dissipation and weak tunnelling. To do so, let us consider the spin-boson problem in equation (93) in the case of a strong coupling between the quasi-spin and the bath degrees of freedom. As a primary effect, the bath oscillators will become shifted due to this coupling to new positions which depend on the spin state. If the tunnelling coupling Δ were *absent*, then the small polaron unitary transformation [1, 11, 166–171]

$$\hat{U} = \exp\left[\frac{1}{2}\hat{\sigma}_z\hat{R}\right], \quad \hat{R} = \sum_\lambda \frac{\kappa_\lambda}{\hbar\omega_\lambda}\left(B_\lambda^\dagger - B_\lambda\right) \tag{100}$$

to the new basis of displaced bath oscillators $B_\lambda^\dagger = U^\dagger b_\lambda^\dagger U = b_\lambda^\dagger + (\kappa_\lambda/2\hbar\omega_\lambda)\hat{\sigma}_z$, $B_\lambda = U^\dagger b_\lambda U = b_\lambda + (\kappa_\lambda/2\hbar\omega_\lambda)\hat{\sigma}_z$ and boson-dressed spin states, $|\tilde{n}\rangle := \hat{U}^\dagger|n\rangle$ would in fact diagonalise the Hamiltonian, solving thereby the problem of finding the eigenstates of the *total* system *exactly*. For this reason, the corresponding canonically transformed basis of phonon-dressed quasi-spin states (polaronic states) and displaced bath oscillators is well suited for an approximate treatment in the case of weak intersite tunnelling and strong system-bath coupling. In this new polaronic basis the Hamiltonian reads,

$$\begin{aligned} H(t) = {} & \frac{1}{2}\hbar\epsilon(t)\left[|\tilde{1}\rangle\langle\tilde{1}| - |\tilde{2}\rangle\langle\tilde{2}|\right] + \frac{1}{2}\hbar\Delta(t)\left(\left\langle e^{\hat{R}}\right\rangle_B|\tilde{1}\rangle\langle\tilde{2}| + \left\langle e^{-\hat{R}}\right\rangle_B|\tilde{2}\rangle\langle\tilde{1}|\right) \\ & + \frac{1}{2}\hbar\Delta(t)\left(\left[e^{\hat{R}} - \left\langle e^{\hat{R}}\right\rangle_B\right]|\tilde{1}\rangle\langle\tilde{2}| + \left[e^{-\hat{R}} - \left\langle e^{-\hat{R}}\right\rangle_B\right]|\tilde{2}\rangle\langle\tilde{1}|\right) \\ & + \frac{1}{2}\sum_\lambda \hbar\omega_\lambda(B_\lambda^\dagger B_\lambda + 1/2) - \lambda\hat{I}/4 \end{aligned} \tag{101}$$

where

$$\lambda = \frac{\hbar}{2\pi}\int_0^\infty \frac{J(\omega)}{\omega}\,d\omega \tag{102}$$

is the reorganisation energy.

Since $\langle\exp[\pm\hat{R}]\rangle_B = \exp[\langle\hat{R}^2\rangle_B/2] = \exp[-D]$, where $D = \frac{1}{4\pi}\int_0^\infty [J(\omega)\coth(\beta\hbar\omega)/\omega^2]d\omega$ and $\beta = 1/(k_B T)$, the effective tunnelling coupling, $\Delta_r := \Delta\exp(-D)$, between the polaronic states is exponentially suppressed by the Debye-Waller factor [11, 167, 168]. For the relevant case of Ohmic coupling, $J(\omega) = 4\pi\alpha\omega\exp(-\omega/\omega_c)$, $D \to \infty$ and $\Delta_r \to 0$ due to the infrared divergence of the corresponding integral. One can attempt to remove this divergence by using instead of κ_λ in the polaron transformation some variational parameters to be determined from the requirement of a minimum of the (free) energy of the whole system [170]. An approximate solution of the corresponding variational problem by using the Peierls-Bogolyubov-Feynman upper bound for the free energy [172, 173] leads [170] to a self-consistent equation for Δ_r which at $T = 0$ and for the symmetric case $\epsilon(t) = 0$ reads,

$$\Delta_r = \Delta\exp\left[-\frac{1}{4\pi}\int_0^\infty \frac{J(\omega)}{(\omega + \Delta_r)^2}\,d\omega\right]. \tag{103}$$

Numerically, it can be solved by iterations. An approximate analytical solution is also available in the limiting case $\omega_c \gg \Delta$ for $\alpha < 1$. It yields the celebrated renormalised tunnelling matrix element, i.e., $\Delta_r = \Delta(\Delta/\tilde{\omega}_c)^{\alpha/(1-\alpha)}$ [1, 2, 170, 174, 175] with $\tilde{\omega}_c = C\omega_c$, where C is some constant which depends on the precise form of cutoff function in $J(\omega)$. In this case, the use of the variationally optimised polaron basis allows one to obtain an effective Bloch-Redfield description which interpolates well between weak and strong dissipation, see for the undriven case the study in [170]. The corresponding generalisation of this approach onto the driven case for an intermediate coupling strength $\alpha < 1$ remains yet to be done. Within our approach this generalisation is rather straightforward.

We proceed further with the case of a strong coupling, i.e. $\alpha \geq 1$, where Δ_r does iterate to zero for any fixed value of ω_c. This fact indicates the famous dissipation-induced localisation transition [1, 174, 175]. In this case, the discussed divergence is not removable; it is real. The polaronic states are strictly localised in this case. This is also the feature that causes the localisation phase transition in the dissipative tight-binding model [2, 176, 177]. The second line in equation (101) presents a (small) time-dependent interaction between the dressed system and the bath which can be handled in perturbation theory in the lowest order of tunnelling coupling Δ. Applying the GME (61) to the considered case of an Ohmic bath yields [67, 101] a GME in the form of equations (79), (80) wherein $f_0(t, t')$ and $g_0(t, t')$ assume, however, a distinct different form; namely,

$$f_0(t, t') = \Delta(t)\Delta(t') \exp[-\mathrm{Re}\, Q(t - t')] \cos[\mathrm{Im}\, Q(t - t')],$$

$$g_0(t, t') = \Delta(t)\Delta(t') \exp[-\mathrm{Re}\, Q(t - t')] \sin[\mathrm{Im}\, Q(t - t')], \tag{104}$$

where

$$Q(t) = \int_0^t dt_1 \int_0^{t_1} K(t_2) dt_2 + i\lambda t/\hbar \tag{105}$$

denotes the doubly-integrated autocorrelation function of the bath, $K(t)$, in equation (69). For $\Delta(t) = const$ the same generalised master equation was derived in [88] using a different approach. It has been derived also in [98] using the path-integral method within the so-called noninteracting blip approximation (NIBA). In the case $\Delta(t) = const$ and $\epsilon(t) = const$, it reduces to the NIBA master equation of [178–180].

Notably, the driven NIBA master equation is valid for $\alpha \geq 1$ at $T = 0$ and $\epsilon_0 = 0$ (and sufficiently small $\Delta \ll \lambda/\hbar = 2\alpha\omega_c$). It can also be used, however, for $\alpha < 1$ for an asymmetric case, $\epsilon_0 \neq 0$, and/or for $T > 0$, where the dynamics (in the absence of driving) is incoherent and where $\Delta_r = 0$. The parameter domain, where this latter condition is fulfilled, is defined from the solution of a (more complicated than equation (103)) self-consistent equation for Δ_r which generally depends on the static bias ϵ_0, temperature T, cutoff ω_c, It can be solved only numerically: in particular, for $\epsilon_0 \neq 0$ and $T = 0$, the renormalised tunnelling coupling vanishes, $\Delta_r = 0$, already for $\alpha > 1/2$. Moreover, even for zero energy bias, $\epsilon_0 = 0$, the renormalised tunnelling coupling vanishes at a sufficiently high temperature, $\pi\alpha k_{BT} > \hbar\Delta$ [170]. Even more, for $\Delta_r \neq 0$, the incoherent tunnelling regime holds obviously when $k_B T \gg \hbar\Delta_r$. Surprisingly, however, for the symmetric situation, $\epsilon_0 = 0$, the NIBA master

equation turns out to be a very good approximation even for arbitrarily small α and T (including coherent dynamics) in the so-called scaling limit $\omega_c \gg \Delta$ with Δ_r fixed. This remarkable fact is rationalised within the path-integral approach [2]. Some understanding can be obtained by observing that in the limit of vanishing dissipation $\alpha \to 0$ the NIBA master equation is exact and it reduces to the one in equation (45), for the initial condition being $\sigma_z(0) = \pm 1$. This, however, amounts to a singular limit which must be handled with care.

6.3.1. Fast fluctuating energy levels. Let us assume for the following an incoherent quantum dynamics with a time-independent tunnelling matrix element $\Delta(t) = const$. In the case of fast stationary fluctuating energy levels the procedure of section 5 leads (after Markovian approximation) to an averaged dynamics in equation (73) with the time-averaged transition rates given by

$$\langle W_{12}(\epsilon_0)\rangle_\epsilon = \frac{1}{2}\Delta^2 \mathrm{Re}\int_0^\infty e^{i\epsilon_0 t - Q(t)}\langle S(t)\rangle_\epsilon \, dt \tag{106}$$

$$\langle W_{21}(\epsilon_0)\rangle_\epsilon = \frac{1}{2}\Delta^2 \mathrm{Re}\int_0^\infty e^{-i\epsilon_0 t - Q(t)}\langle S^*(t)\rangle_\epsilon \, dt, \tag{107}$$

where,

$$\langle S(t)\rangle_\epsilon := \langle S(t+t_0, t_0)\rangle_\epsilon = \left\langle e^{i\int_{t_0}^{t+t_0}\tilde{\epsilon}(t')dt'}\right\rangle_\epsilon \tag{108}$$

is the averaged propagator of the corresponding Kubo oscillator which does not depend anymore on the initial time t_0, or the initial phase of driving. These averaged rates can be also given in the equivalent spectral representation form, like in equation (74),

$$\begin{aligned}\langle W_{12}(\epsilon_0)\rangle_\epsilon &= \frac{\pi}{2}\Delta^2\int_{-\infty}^{\infty} FC(\omega)I(\epsilon_0-\omega)d\omega,\\ \langle W_{21}(\epsilon_0)\rangle_\epsilon &= \frac{\pi}{2}\Delta^2\int_{-\infty}^{\infty} e^{-\hbar\omega/k_BT}FC(\omega)I(\epsilon_0-\omega)d\omega,\end{aligned} \tag{109}$$

where

$$FC(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\exp[i\omega t - Q(t)]dt \tag{110}$$

is the Franck-Condon factor[18] which describes spectral line shape due to multi-phonon transitions [8, 181, 182], and $I(\omega)$ denotes the spectral line shape of the Kubo oscillator, $\dot{X}(t) = i\tilde{\epsilon}(t)X(t)$. The result in equation (106) is in essence the Golden Rule result generalised here to fast fluctuating nonequilibrium fields. This fact underlines the generality and importance of the *nonequilibrium* Golden Rule result which is very useful in many applications. Many profound nonequilibrium

[18] i.e. the thermally weighted overlap of the wave functions of displaced quantum oscillators.

effects described in this work can be rationalised within its framework. The structure of this result has a clear physical interpretation. Namely, $FC(\omega)$ in (110) is nothing but the spectral line shape of a *quantum* Kubo oscillator with the frequency modulated by the quantum Gaussian force $\hat{\xi}(t)$ in equation (68) (in the corresponding Heisenberg representation) which has the complex-valued equilibrium autocorrelation function in equation (69). Due to the Gaussian character of the quantum random force, this spectral line shape in equation (110) is expressed merely in terms of the doubly-integrated autocorrelation function $K(t)$ and the reorganisation energy term in equation (105). Due to the equilibrium character of quantum fluctuations, $FC(\omega)$ possesses a symmetry property, $FC(-\omega) = e^{-\beta\hbar\omega}FC(\omega)$, which is enforced by the thermal detailed balance condition. It holds independently of the form of the bath spectral density $J(\omega)$ [1]. Thus, the thermal equilibrium for *localised* energy levels,[19] $p_1(\infty) = e^{-\hbar\epsilon_0/k_BT}p_2(\infty)$, holds always in the absence of *nonequilibrium* fluctuations of the energy levels. Furthermore, by splitting $\hat{\xi}$ into a sum of two arbitrary statistically independent components (two subsets of quantum bath oscillators), $\hat{\xi} = \hat{\xi}_1 + \hat{\xi}_2$ one can show that $FC(\omega)$ can exactly be represented as a frequency convolution of the corresponding (partial) Franck-Condon factors $FC_1(\omega)$ and $FC_2(\omega)$ [2, 8], namely,

$$FC(\epsilon) = \int_{-\infty}^{\infty} FC_1(\omega)FC_2(\epsilon - \omega)d\omega. \tag{111}$$

Such frequency convolution can be generalised to an arbitrary number of partitions. The *nonequilibrium* Golden Rule in equation (109) presents an additional frequency convolution with the spectral line shape $I(\omega)$ of the *nonequilibrium* Kubo oscillator which corresponds to a generally non-Gaussian and nonequilibrium stochastic force. $I(\omega)$ does now no longer possess the above symmetry imposed by thermal detailed balance. Thus, the violation of the thermal detailed balance condition by the nonequilibrium fluctuations lead generally to intriguing nonequilibrium effects described in section 5, and below. It is important to notice that the localised states can be stabilised by strong, fast oscillating periodic fields [183] and the Golden Rule description is generally improved for such fields [97]. This latter fact can be readily understood from the representation of the (quantum) stochastic force as a sum of statistically independent components. Namely, if $\Delta_r = 0$, due the interaction with a subset of oscillators, the addition of an interaction with further oscillators cannot enhance Δ_r. It will work always in the direction to make the effective tunnelling coupling smaller (when $\Delta_r \neq 0$), thus improving the perturbation theory in Δ. Replacing equilibrium oscillators with a fast fluctuating field does not change this trend.

6.3.2. Exact averaging over dichotomous fluctuations of the energy levels. An exact averaging of the NIBA master equation of the driven spin-boson model in the dichotomous Markovian field is possible by analogy with the consideration pursued in section 5.4. The result is formally the same as in equation (85) with $f_0(t - t')$ and $g_0(t - t')$ given but in equation (104) (with $\Delta(t) = const$) [101]. An interesting feature

[19]Reminder: we consider the case $\Delta_r = 0$, or $k_BT \gg \hbar\Delta_r$.

is that for $\epsilon_0 = 0$ the equations for the average $\langle\sigma_z(t)\rangle$ and the correlator $\langle\alpha(t)\sigma_z(t)\rangle$ are decoupled. Moreover, in the dissipation-free case, $Q(t) = 0$, the solution of equation for $\langle\sigma_z(t)\rangle$ with the initial condition $\langle\sigma_z(0)\rangle = 1$ yields the same result as in equation (40) with the following substitutions implemented, i.e., $\langle\sigma_z\rangle \to \langle\sigma_x\rangle$, $\sigma \to \Delta$, $\Delta \to \epsilon_0$. This finding provides a rather nontrivial cross-check of the validity of different methods of stochastic averaging.

6.3.3. Electron transfer in fast oscillating periodic fields. Let us next focus on the case with strong and fast periodic driving fields $\tilde{\epsilon}(t) = A\cos(\Omega t + \varphi_0)$, yielding

$$\langle W_{12}(\epsilon_0)\rangle_\epsilon = \frac{\pi}{2}\Delta^2 \sum_{n=-\infty}^{\infty} J_n^2\Big(\frac{A}{\Omega}\Big) FC(\epsilon_0 - n\Omega),$$

$$\langle W_{21}(\epsilon_0)\rangle_\epsilon = \frac{\pi}{2}\Delta^2 \sum_{n=-\infty}^{\infty} J_n^2\Big(\frac{A}{\Omega}\Big) e^{-\hbar[\epsilon_0 - n\Omega]/k_BT} FC(\epsilon_0 - n\Omega). \tag{112}$$

This result of the Golden Rule type for the nonadiabatic ET rates in strong periodic fields has been derived in [83] and independently in [89]. In particular, the quasi-static (Gaussian) approximation for $FC(\omega)$ for $k_BT \gg \hbar\omega_c$ with $K(t)$ replaced by $K(0) \approx 2k_BT\lambda/\hbar^2$ in equation (105) leads in absence of driving, i.e. $A = 0$, independent of the detailed structure of $J(\omega)$, to the celebrated Marcus–Dogonadze–Levich rate expression [184, 185] for the ET rates with

$$FC(\omega) = \frac{\hbar}{\sqrt{4\pi\lambda k_BT}} \exp\Big(-\frac{(\hbar\omega - \lambda)^2}{4\lambda k_BT}\Big). \tag{113}$$

This approximation is suitable for a thermal bath with a low frequency cut-off and in the high-temperature limit, e.g., for polar solvents. This presents a semiclassical limit for the Franck-Condon factor. If some high-frequency (quantum) vibrational mode ω_0 couples to ET with the coupling constant κ_0 in addition to the low-frequency vibrations, being of relevance for ET in molecular aggregates, then a different model for $FC(\omega)$ is more appropriate, namely [8, 186],

$$FC(\omega) = \frac{\hbar}{\sqrt{4\pi\lambda k_BT}} e^{-D_0} \sum_{p=-\infty}^{\infty} I_{|p|}(x) e^{-p\hbar\omega_0/2k_BT} \exp\Big(-\frac{(\hbar\omega - \lambda + p\hbar\omega_0)^2}{4\lambda k_BT}\Big) \tag{114}$$

where $S = (\kappa_0/\hbar\omega_0)^2$, $D_0 = S\coth(\hbar\omega_0/2k_BT)$, $x = S/\sinh(\hbar\omega_0/2k_BT)$, and $I_p(x)$ is the modified Bessel function. The periodic driving may induce an inversion of ET transfer direction and modulate the ET transfer rates by orders of magnitude. This has been theoretically predicted in [83, 89] for both of the above-mentioned models of $FC(\omega)$.[20]

[20]The use of an improved perturbation theory in Δ in the case of fast fluctuating fields does *not* imply that the Golden Rule rates cannot be enhanced by such *nonequilibrium* fields. A large enhancement of the forward (backward) rate can occur, e.g., when the absorption of n photons helps to overcome the corresponding forward (backward) activation barrier of the thermally-assisted incoherent tunnelling. For example, for the generalised Marcus rates a condition is $\epsilon_0 \mp \lambda/\hbar \pm n\hbar\Omega = 0$, with the field amplitude A chosen such that the probability $J_n^2(A/\Omega)$ of the corresponding reaction channel is maximised.

6.3.4. Dichotomously fluctuating tunnelling barrier. Another relevant situation involves the case of fluctuating tunnelling matrix element $\Delta(t)$ and constant energy bias $\epsilon(t) = \epsilon_0 = const$. In the superexchange picture of ET this corresponds to a physical situation where the stochastic dynamics of the bridge states, which mediate the ET between the donor and acceptor molecules, introduces an explicit, stochastic time-dependence into $\Delta(t)$. Generically, this corresponds to a fluctuating tunnelling barrier. In the case of dichotomous Markovian fluctuations $\Delta(t) = \Delta_0 + \Delta\alpha(t)$, the stochastic averaging of the NIBA master equation can be done exactly [67]. Towards this goal one makes use of the Shapiro-Loginov theorem (83) and the following exact decoupling property [152, 153, 187]:

$$\langle \alpha(t)\alpha(t')\sigma_z(t')\rangle = \langle \alpha(t)\alpha(t')\rangle\langle \sigma_z(t')\rangle. \tag{115}$$

Applying these two theorems and using the DMP property, $\alpha^2(t) = 1$, the averaging of the GME yields the following exact results [67]:

$$\begin{aligned}\frac{d}{dt}\langle \sigma_z(t)\rangle = &-\int_0^t \Big([\Delta_0^2 + \Delta^2 e^{-\nu(t-t')}]\, f(t-t')\langle \sigma_z(t')\rangle + \Delta_0\Delta[1 + e^{-\nu(t-t')}] \\ &\times f(t-t')\langle \alpha(t')\sigma_z(t')\rangle + [\Delta_0^2 + \Delta^2 e^{-\nu(t-t')}] g(t-t') \Big) dt', \\ \frac{d}{dt}\langle \alpha(t)\sigma_z(t)\rangle = &-\nu\langle \alpha(t)\sigma_z(t)\rangle - \int_0^t \Big([\Delta^2 + \Delta_0^2 e^{-\nu(t-t')}] f(t-t')\langle \alpha(t')\sigma_z(t')\rangle \\ &+ \Delta_0\Delta[1 + e^{-\nu(t-t')}]\{ f(t-t')\langle \sigma_z(t')\rangle + g(t-t')\} \Big) dt',\end{aligned} \tag{116}$$

where

$$\begin{aligned} f(t) &= \exp[-\mathrm{Re}\, Q(t)]\cos[\mathrm{Im}\, Q(t)]\cos[\epsilon_0 t], \\ g(t) &= \exp[-\mathrm{Re}\, Q(t)]\sin[\mathrm{Im}\, Q(t)]\sin[\epsilon_0 t]. \end{aligned} \tag{117}$$

For the case of vanishing dissipation, $Q(t) = 0$, and for $\Delta_0 = 0$, the solution of this integro-differential equation for $\langle \sigma_z(t)\rangle$ for the initial condition $\langle \sigma_z(0)\rangle = 1$ yields the same result as in equation (35). This agreement provides an additional test for the mutual consistency of different methods of stochastic averaging used here.

Furthermore, in the absence of dissipation the rate of incoherent relaxation exhibits a resonance-like feature as a function of the frequency ν of the barrier fluctuations. Namely, a resonance occurs when ν matches the transition frequency ϵ_0, i.e. $\nu = \epsilon_0$ (see equation (37) in section 2.3.2). This presents a physical stochastic resonance, which should not to be identified with a well-known phenomenon of noise-assisted Stochastic Resonance [188]. It occurs when a stochastic frequency of the driving matches an eigenfrequency of a quantum transition. In the presence of dissipation, this resonance feature is maintained, but becomes modified. Namely, the resonance can occur at $\nu = |\epsilon_0 \pm \lambda/\hbar|$, rather than at $\nu = \epsilon_0$ [67]. This resonance is responsible for the interesting phenomenon of a stochastic acceleration of dissipative quantum tunnelling which is predicted by the theory [67]: For the case that $\Delta := \Delta_0$, when $\Delta(t)$ fluctuates between zero and $2\Delta_0$ the rate of incoherent transfer can exceed that for the static tunnelling barrier with tunnelling coupling strength $\Delta(t) = 2\Delta_0 = \mathrm{const}$. At the first sight, this effect seems paradoxical; it must be remembered, however, that the considered noise is *nonequilibrium* and it is capable

of pumping energy into the system enhancing thereby the rate of incoherent quantum tunnelling. Unfortunately, for the parameters typical for molecular ET the experimental conditions for this effect to occur can barely be met experimentally because the required frequency ν is too high. Nevertheless, this fact does not invalidate the principal possibility of the discussed effect for some other physical systems in view of the generality of the model set-up.

In contrast, when $\Delta(t)$ fluctuates very slowly on the time-scale of decay of kernels $f(t)$ and $g(t)$, which corresponds roughly to the inverse of the width of corresponding Franck-Condon factor $FC(\omega)$, then our theory predicts – after use of the Markovian approximation – the known results which corresponds to the approximation of a dichotomously fluctuating rate [189], see also discussion in section 5.3. The corresponding problem of such fluctuating rates is known under the label of *dynamical disorder* and can be met in quite different areas of physics and chemistry [190]. Depending on the relation between the stochastic frequency ν and the values of transfer rates corresponding to the "frozen" instant realisations of $\Delta(t)$, the transfer kinetics can exhibit different regimes of a (i) quasi-static disorder, (ii) an averaged rate description, and (iii) a gated regime [67]. In the latter case, the mean transfer time becomes locked to the autocorrelation time of the fluctuations [68, 191].

The influence of strong laser fields on the ET with nonequilibrium dynamical disorder [86], or driven by nonequilibrium conformational fluctuations [68] has been studied within the obtained NIBA master equation approach in [68, 86]. In particular, it has been shown there, that a strong periodic field can induce a turnover between the nonadiabatic regime of electron transfer and a gated regime. Moreover, the direction of ET in the gated regime can be inverted, whereas the mean transfer time remains chiefly controlled by the nonequilibrium stochastic fluctuations and it is not influenced by periodic field [86]. These theoretical predictions discussed here are still awaiting their experimental realisation. The area of chemically gated, or chemically driven electron transfer [192], that is the ET controlled by nonequilibrium fluctuations due to spontaneous release of energy by breaking some energy-rich chemical bonds (e.g., due to the ATP hydrolysis), is currently still in its infancy [192].

7. Quantum transport in dissipative tight-binding models subjected to strong external fields

A salient application of our theoretical efforts relates to charge and particle transfer in spatially extended molecular structures. It can be described within a model similar to the Holstein model of a molecular crystal [167, 193]. Namely, one considers a molecular chain using the assumption that only one energy, namely, a lowest unoccupied molecular orbital (LUMO)-level describes the ET (or highest occupied, HOMO-level in case of a hole transport) per molecule, or molecular group. These energy levels are coupled to the local intramolecular vibrations which are thermalised. The transferring particle is delocalised due to a tunnelling coupling between the nearest neighbours. The intersite coupling between the intramolecular vibrations is however neglected (like in the Einstein model of optical phonons), i.e. the electron (or hole) energy levels in neighbouring molecules (or molecular groups) are assumed

to fluctuate independently. In other words, one assumes uncorrelated identical thermal baths formed by vibrational degrees of freedom of each molecule in a molecular chain. Such a model is close in spirit to one used for exciton transfer within a stochastic Langevin description [40]. In the approximations employed below, this model becomes equivalent to the model of a Quantum Brownian Motion within a single band, tight-binding description. In an external electric field $\mathcal{E}(t)$, the latter one reads [3, 4]:

$$H_{\rm TB}(t) = -\frac{\hbar\Delta}{2}\sum_{n=-\infty}^{\infty}(|n\rangle\langle n+1| + |n+1\rangle\langle n|) - e\mathcal{E}(t)\hat{x} + H_{\rm BI}, \tag{118}$$

$$H_{\rm BI} = \frac{1}{2}\sum_i\left[\frac{\hat{p}_i^2}{m_i} + m_i\omega_i^2\left(\hat{q}_i - \frac{c_i}{m_i\omega_i^2}\hat{x}\right)^2\right],$$

where $\hat{x} = a\sum_n n|n\rangle\langle n|$ is the operator of the coordinate (within the single band description). The model in equation (118) can be derived from a different perspective than the Holstein model, namely, by starting out from a model of Quantum Brownian Motion in a periodic potential [2, 3, 80] and by restricting the corresponding consideration to the lowest band for the tunnelling particle in the deep quantum regime. We consider this model in the limit of a strong coupling by applying the small polaron transformation which now reads $\hat{U} = \exp[-i\hat{x}\hat{P}/\hbar]$, $\hat{P} = \sum_i c_i\hat{p}_i/\ (m_i\omega_i^2)$. In the polaron basis, the Hamiltonian reads

$$H_{\rm TB}(t) = -\frac{\hbar\Delta_r}{2}\sum_{n=-\infty}^{\infty}(|\tilde{n}\rangle\langle\tilde{n}+1| + |\tilde{n}+1\rangle\langle\tilde{n}|) - e\mathcal{E}(t)\hat{x}$$
$$-\sum_{n=-\infty}^{\infty}(\hat{\xi}|\tilde{n}\rangle\langle\tilde{n}+1| + h.c.) + \frac{1}{2}\sum_i\left[\frac{\hat{p}_i^2}{m_i} + m_i\omega_i^2\tilde{Q}_i^2\right], \tag{119}$$

where $\Delta_r = \Delta\langle e^{-ia\hat{P}/\hbar}\rangle_B = \Delta e^{-a^2\langle\hat{P}^2\rangle_B/2\hbar^2}$ is the renormalised tunnelling coupling (polaron band width), $\tilde{Q}_i := \hat{U}q_i\hat{U}^{-1} = \hat{q}_i - (c_i/m_i\omega_i^2)\hat{x}$ are displaced bath oscillators and $\hat{\xi} = \frac{\hbar}{2}[\Delta e^{-ia\hat{P}/\hbar} - \Delta_r]$ is the quantum random force operator in the polaron basis which is considered further as a small perturbation. Note that $\hat{x}$ is not changed. Assuming a strong Ohmic dissipation with $\alpha \geq 1$ yields $\Delta_r = 0$ at $T = 0K$ and for $\mathcal{E}(t) = 0$. This indicates the celebrated localisation phase transition [176, 177], which alternatively can also be interpreted as a polaron band collapse. In the presence of a constant electric field and/or for $T > 0$ this localisation transition occurs for smaller values of α. Given our case of strong coupling, the transport occurs predominantly via incoherent tunnelling hops between the nearest sites of localisation. As a side remark, we note that also in the dissipation-free case the Bloch band can collapse in presence of strong periodic fields [194], known as the effect of dynamical localisation [195]. Use of equation (61) for the case in (119) with $\Delta_r = 0$ yields for the diagonal elements of the reduced density matrix a set of coupled generalised master equations

$$\dot{\rho}_{nn}(t) = \int_0^t\Big\{W^{(+)}(t,\tau)\rho_{n-1n-1}(\tau) + W^{(-)}(t,\tau)\rho_{n+1n+1}(\tau)$$
$$-[W^{(+)}(t,\tau) + W^{(-)}(t,\tau)]\rho_{nn}(\tau)\Big\}d\tau \tag{120}$$

with memory kernels

$$W^{(\pm)}(t,\tau) = \frac{1}{2}\Delta^2 e^{-\mathrm{Re}\,Q(t-\tau)} \cos\left[\mathrm{Im}\,Q(t-\tau) \mp \frac{ea}{\hbar}\int_\tau^t \mathcal{E}(t')dt'\right]. \tag{121}$$

The very same equations are obtained in the NIBA approximation of the path-integral approach [196]. The Holstein-like model which has been discussed at the beginning of this section yields in similar approximations the same set of GMEs (with a trivial renormalisation of the coupling constant in the identical bath spectral densities $J_n(\omega) = J(\omega)$) [69]. The stationary electrical current carried by one particle reads $j = e\lim_{t\to\infty}\frac{d}{dt}\langle x(t)\rangle$, where $\langle x(t)\rangle = a\sum_n n\rho_{nn}(t)$ denotes the mean particle position in the considered infinite chain. It obeys (this result follows immediately from equation (120))

$$\frac{d}{dt}\langle x(t)\rangle = a\int_0^t \left[W^+(t,\tau) - W^-(t,\tau)\right]d\tau. \tag{122}$$

This current in (122) still needs to be averaged of the stochastic field realisations.[21] This objective is again reduced to the averaging of an effective Kubo oscillator which can be done exactly for many different models of stochastic driving. We decompose the electric field $\mathcal{E}(t)$ into the sum of the mean, or constant field $\mathcal{E}_0$ and a fluctuating, unbiased component $\tilde{\mathcal{E}}(t)$, i.e. $\mathcal{E}(t) = \mathcal{E}_0 + \tilde{\mathcal{E}}(t)$. The resulting expression for the averaged current $j(\mathcal{E}_0)$ can be put into two equivalent forms. First, it can be written in terms of a time integral [70, 102],

$$j(\mathcal{E}_0) = ea\Delta^2\int_0^\infty \exp[-\mathrm{Re}\,Q(\tau)]\sin[\mathrm{Im}\,Q(\tau)]\mathrm{Im}[e^{iea\mathcal{E}_0\tau/\hbar}\langle S(\tau)\rangle]d\tau, \tag{123}$$

where $\langle S(\tau)\rangle$ is given in equation (108) with $\tilde{\epsilon}(t) = ea\tilde{\mathcal{E}}(t)/\hbar$ and $Q(t)$ in equation (105). Alternatively, the current expression can be given as a frequency convolution in a spectral representation form, i.e.,

$$j(\mathcal{E}_0) = \int_{-\infty}^\infty j_{dc}(\omega)I(ea\mathcal{E}_0/\hbar - \omega)d\omega, \tag{124}$$

where

$$j_{dc}(\omega) = \frac{\pi}{2}ea\Delta^2\left(1 - e^{-\hbar\beta\omega}\right)FC(\omega). \tag{125}$$

$I(\omega)$ denotes the spectral line shape corresponding to $\langle S(\tau)\rangle$. The dc-current obeys the symmetry property $j_{dc}(-\omega) = -j_{dc}(\omega)$ which is imposed by the thermal detailed balance symmetry, $FC(-\omega) = e^{-\hbar\beta\omega}FC(\omega)$ with $FC(\omega)$ in (110). It is important to note that the averaged current in (124) does not obey such a symmetry requirement.

7.1. *Noise-induced absolute negative mobility*

As a first application of the above results we consider the phenomenon of ANM, or absolute negative mobility, where the transferring particles move around *zero bias* in

[21] In the case of periodic driving, this additional averaging is obsolete by defining the current in a self-averaged manner as $j = e\lim_{t\to\infty}\langle x(t)\rangle/t$.

opposite direction to the average applied force. This effect was anticipated for semiconductors in strong periodic fields almost thirty years ago using a Boltzmann equation approach [197, 198]. The first experimental realisation was obtained in 1995 for semiconductor superlattices [199]. The corresponding experimental results were seemingly consistent [199] with a mechanism of incoherent sequential tunnelling like one just described. The occurrence of the ANM phenomenon for a sinusoidal driving within the considered dissipative tight-binding model has been demonstrated in [196].

The question we addressed in [69] within a Holstein-like model was whether an external stochastic field can also induce ANM. The occurrence of such noise-induced ANM has been shown for dichotomous Markovian fields. ANM presents a multi-state analogy of the effect of inversion of populations in TLS described in section 5. A simple criterion for ANM to occur can be found within the quasi-static approximation for the spectral line shape $I(\omega)$. For a symmetric dichotomous field $\tilde{\mathcal{E}}(t) = (\hbar\sigma/ea)\alpha(t)$ with the inverse autocorrelation time ν, this quasi-static approximation holds whenever $\sigma \gg \nu$, being almost always the case in the relevant regime of parameters even if the field fluctuations are fast on the time-scale of the charge transfer. Then, $I(\omega) \approx \frac{1}{2}[\delta(\omega-\sigma)+\delta(\omega-\sigma)]$ and $j(\mathcal{E}_0) = \frac{1}{2}[\, j_{dc}(ea\mathcal{E}_0/\hbar-\sigma) + j_{dc}(ea\mathcal{E}_0/\hbar+\sigma)]$.

Given the symmetry property, $j_{dc}(-\sigma) = -j_{dc}(\sigma)$, one can conclude that the phenomenon of ANM will occur in *any* such system with the static current–voltage characteristics $j_{dc}(\sigma)$ assuming a maximum at some σ_{max} which is complemented by a corresponding regime of *differential* negative conductance occurring for $\sigma > \sigma_{max}$. Then, $j(\mathcal{E}_0) < 0$ for a sufficiently small static force, $e\mathcal{E}_0 > 0$, whenever $\sigma > \sigma_{max}$ [69], i.e. whenever the charge transfer is driven into the regime of negative differential conductance by some appropriately chosen alternating, two-state stochastic fields. This mechanism is quite general and robust. It does not depend on the details of the dissipation mechanism. In particular, for the Gaussian $FC(\omega)$ in equation (113), we obtain

$$j_{dc}(ea\mathcal{E}_0/\hbar) = \frac{\pi}{2}\frac{ea\Delta^2\hbar}{\sqrt{\pi\lambda k_B T}}\exp\left[-\frac{\lambda^2+(ea\mathcal{E}_0)^2}{4\lambda k_B T}\right]\sinh\left[\frac{ea\mathcal{E}_0}{2k_B T}\right]. \tag{126}$$

This corresponds to a (nonadiabatic) small polaron conductance [167, 200] with the differential mobility, $\mu(\mathcal{E}_0) = dv(\mathcal{E}_0)/d\mathcal{E}_0$, obeying in the linear response range

$$\mu(0) = \sqrt{\frac{\pi}{2W_p}}\frac{ea^2V^2}{\hbar(k_BT)^{3/2}}e^{-W_p/2k_BT}, \tag{127}$$

where $W_p = \lambda/2$ is the polaron binding energy and $V = \hbar\Delta/2$. For this nonadiabatic small polaron model the regime of negative differential mobility occurs for $\mathcal{E}_0 > \mathcal{E}_{max}$ with $\mathcal{E}_{max}$ defined implicitly by the equation $ea\mathcal{E}_{max} = 2W_p\coth(ea\mathcal{E}_{max}/2k_BT)$. Quasi-one-dimensional systems exhibiting this small polaron conductance (in the nonadiabatic ET regime with respect to Δ) can be considered along with the semiconductor superlattices as possible candidates to exhibit the phenomenon of noise-induced ANM experimentally. A finite photo-induced small polaron mobility of the hole type is found, for example, in columnar liquid crystals [201–203]. We then estimate the value of $\mathcal{E}_{max}$ for these systems with the lattice period of about

$a = 0.35$ nm to be in the range of 5×10^6 V/cm, which is rather large. For superlattices with a larger period a, $\mathcal{E}_{max}$ can be much less [199]. Basically, this crucial quantity is determined by two factors: (i) the width of $FC(\omega)$ due to multi-phonon transitions (it depends on the precise mechanism of dissipation and should be made as small as possible) and (ii) the lattice period a (it should be engineered as large as possible). These criteria can serve as a useful guides in identifying the appropriate experimental materials.

7.2. *Dissipative quantum rectifiers*

Yet another intriguing application is provided by the fluctuation-induced quantum transport in the *absence* of a mean electric field, $\mathcal{E}_0 = 0$. Similar nonequilibrium phenomena are known under the notion of Brownian motors, or Brownian ratchets [71–81]. The first case of a quantum ratchet in a periodic spatially asymmetric (ratchet)-potential was studied theoretically in [204] within a semi-classical approach and for an adiabatically varying driving field. In [70, 102, 104], we put forward periodic dissipative nonadiabatic quantum rectifiers [209] operating in the absence of spatial asymmetry. The current is produced by a nonlinear transport mechanism due to an interplay between equilibrium quantum fluctuations and an unbiased, but asymmetric nonequilibrium external noise [70]. Likewise, an asymmetric periodic driving of the harmonic mixing type can be used instead of the nonequilibrium noise [102, 104]. Our rectifier behaves genuinely quantum mechanically and corresponds to the case of a strong dissipation when the transport mechanism is incoherent and the transport proceeds by incoherent tunnelling hopping as outlined above. The origin of the resulting current can be traced to equation (123) and equation (124). Namely, $j(0) \neq 0$, when $\langle S(\tau)\rangle$ assumes complex values, i.e., $\mathrm{Im}\langle S(\tau)\rangle \neq 0$. This corresponds to a complementary criterion which follows from equation (124), namely, $j(0) \neq 0$, when the corresponding spectral line $I(\omega)$ is asymmetric, $I(-\omega) \neq I(\omega)$.

In particular, this is the case of asymmetric dichotomous field of zero mean, cf. section 2.3.1 and equation (28), which takes on the (frequency scaled) two discrete values $ea\tilde{\mathcal{E}}_{1,2}/\hbar = \epsilon_{1,2} = \mp\sigma e^{\mp b/2}$, where b characterises the field asymmetry and σ is the (scaled) rms of field fluctuations. The emergence of a finite current in this case can readily be seen in the quasi-static approximation of $I(\omega)$ for $\sigma \gg \nu$, $I(\omega) \approx p_1\delta(\omega - \sigma e^{-b/2}) + p_2\delta(\omega + \sigma e^{b/2})$ with $p_{1,2} = |\epsilon_{2,1}|/(|\epsilon_1| + \epsilon_2)$. In this adiabatic (with respect to driving) approximation,

$$j(0) = p_2 j_{dc}(\sigma e^{b/2}) - p_1 j_{dc}(\sigma e^{-b/2}). \tag{128}$$

In the semiclassical high-temperature approximation for $FC(\omega)$ in equation (113) (this corresponds to noise-driven small polaron transport), one can see that the rectification current appears as a nonlinear response to the external, unbiased on average driving. Namely, to the lowest order, the current is proportional to $\langle \mathcal{E}^3(t)\rangle$, $j(0) \propto \langle \mathcal{E}^3(t)\rangle \approx b\sigma^3$ ($b \ll 1$), with a nontrivial prefactor. Moreover, the current flows into the direction of $\langle e^3\mathcal{E}^3(t)\rangle$, which is the direction of the larger force realisation, if the applied random force is sufficiently small. With an increase of the noise rms σ the current can however *reverse* its direction. In the considered approximations and for a small driving asymmetry $b \ll 1$ this occurs when σ exceeds some maximum

associated with $FC(\omega)$. Thus, this change of the current direction from the expected to physically counter-intuitive direction is closely related to the mechanism of noise-induced absolute negative mobility, as was outlined in the previous subsection.

Moreover, the current can flow in the physically counter-intuitively direction also for small applied forces when the coupling strength α is sufficiently small. For $T = 0$ a very insightful approximate analytical expression can be obtained in the adiabatic limit for driving and in the lowest order of the asymmetry parameter b. Namely, assuming an Ohmic friction mechanism for the thermal bath with an exponential cutoff ω_c, $FC(\omega)$ can be exactly evaluated at $T = 0$ to yield $FC(\omega) = (1/\omega_c\Gamma(2\alpha)) \times (\omega/\omega_c)^{2\alpha-1} \exp[-\omega/\omega_c]\Theta(\omega)$, where $\Theta(\omega)$ is the Heaviside step function [2]. For $b \ll 1$ in (128), this then yields the averaged, zero bias current value, reading for $\alpha > 1/2$:

$$j(0) \approx b\frac{\pi}{2}\frac{ea\Delta^2}{\omega_c\Gamma(2\alpha)}\left(\frac{\sigma}{\omega_c}\right)^{2\alpha-1}\left(\alpha - 1 - \frac{\sigma}{2\omega_c}\right)\exp(-\sigma/\omega_c). \tag{129}$$

The result in equation (129) predicts that for $\alpha \leq 1$ the current flows into the physically counter-intuitive direction. Furthermore, for $\alpha > 1$, the rectification current flows first in the expected, natural direction, but it changes subsequently its direction for $\sigma > \sigma_* = 2(\alpha - 1)\omega_c$. Moreover, the absolute value of current has two maxima at $\sigma_{max} = (2\alpha - 1 \pm \sqrt{2\alpha - 1})\omega_c$ for $\alpha > 1$ and one maximum at $\sigma_{max} = (2\alpha - 1 + \sqrt{2\alpha - 1})\omega_c$ for $1/2 < \alpha \leq 1$. Furthermore, the current diminishes for large σ. In the low-temperature limit, all these features are in the remarkable agreement with the numerical evaluation of equation (123) in [70]. A related comparison is provided in figure 7 for $\alpha = 2$. For $k_BT = 0.01\hbar\omega_c$, the agreement is indeed excellent, except for very small values $\hbar\sigma \ll k_BT$. On the scale of σ variation used in figure 7 the rectification tunnel current seems be maximal at $T = 0$ for most σ. From this point of view, the rectification results from an interplay between the zero-point

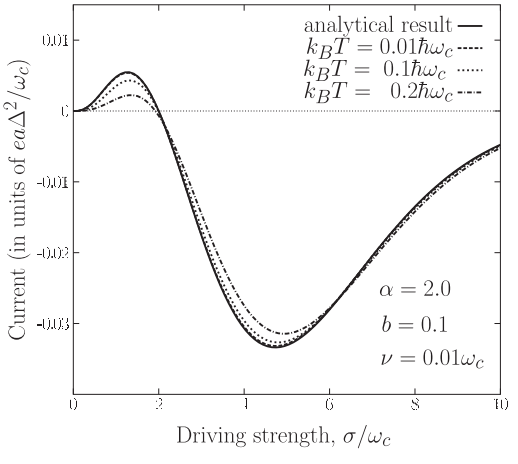

Figure 7. Noise induced rectification of current for an asymmetric dichotomous driving field *vs*. rms of field fluctuations at different temperatures. The set of used parameters is indicated in the figure.

quantum fluctuations and the nonequilibrium noise, i.e. has a manifestly quantum origin.

For larger values of α than those depicted in figure 7, the rectification current can be enhanced for sufficiently small σ/ω_c by increasing temperature and go through a maximum, exhibiting thereby the phenomenon of Quantum Stochastic Resonance [205–208] in the nonlinear current response [70].

7.3. *Limit of vanishing dissipation*

In the limit of vanishing dissipation $Q(t) \to 0$, the result in equation (123) predicts that $j(0) = 0$, independently of the form and strength of driving. This prediction should be considered, however, with care since the result in equation (123) is not valid for very small α and T, because we have assumed throughout incoherent transport regime where either $\Delta_r = 0$, or the temperature is sufficiently high, $k_B T \gg \hbar\Delta_r$. Nevertheless, the dissipationless single-band, infinite tight-binding model can be solved exactly in arbitrary time-dependent fields [70, 103, 104, 195, 210, 211]. The corresponding exact solution for the current then shows [70, 103, 104] that the *stationary* current is forced to vanish identically by the stochastic fluctuations of driving. Put differently, in the absence of quantum dissipation such a rectified current can exist at most as a transient phenomenon. As a matter of fact, the *stationary* rectification current within the single-band tight binding description is due to a nonlinear interplay of quantum dissipation and external nonequilibrium forces. Its origin presents a highly nonlinear and nonequilibrium *statistical effect*. This result does not hold for more general situations. For the case of the full potential problem, with its intrinsic interband transitions, a finite, stationary current can be generated even in the absence of dissipation; it results as a *dynamical effect* due to an interplay of a nonlinear dynamics and the breaking of some space-time symmetries by the driving mechanism [103, 212, 213].

It must be emphasised, however, that the full potential problem has little relation to the electron transport in molecular chains which is our main focus here. This is because the tight-binding description emerges for the electron (or hole) transport processes in molecular systems in a very different way, being not the result of a truncation of a full potential problem to the description within the lowest band only.

7.4. *Case of harmonic mixing drive*

Another instance of quantum rectifiers in presence of dissipation is realised with a harmonic mixing driving [102, 214, 215],

$$\mathcal{E}(t) = E_1 \cos(\Omega t) + E_2 \cos(2\Omega t + \phi), \tag{130}$$

with the driving strengths E_1, E_2, angular frequency Ω and a relative phase ϕ, respectively. This model seems more promising and readily can be implemented with experimental realisations.

The corresponding expression for $\langle S(\tau)\rangle$ reads [102]

$$\langle S(\tau)\rangle = \sum_{k=-\infty}^{\infty} J_{2k}\big(2\xi_1 \sin(\Omega\tau/2)\big) J_k\big(\xi_2 \sin(\Omega\tau)\big) e^{-ik(\phi+\pi/2)}, \tag{131}$$

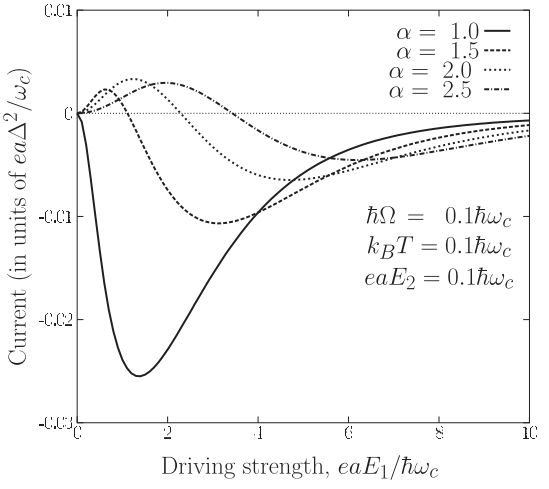

Figure 8. The rectified quantum current induced by a harmonic mixing drive is depicted *vs.* the strength of the first harmonic at different values of the coupling strength α. The strength of the second harmonic is held fixed. The used parameters are given in the figure.

where $\xi_{1,2} = eaE_{1,2}/(\hbar\Omega)$ and $J_n(z)$ are standard Bessel functions. With its help the current in equation (123) can be evaluated numerically for the Ohmic model with the exponential cutoff, where the exact analytical expression for $Q(t)$ is available [2, 3, 69]. Independent of other parameters, the current vanishes identically for $\phi = \pi/2, 3\pi/2$, where $\mathrm{Im}\langle S(\tau)\rangle = 0$ *exactly*. Otherwise, the current can be different from zero. For sufficiently high temperatures and weak fields applied, $j(0) \propto \langle \mathcal{E}^3(t)\rangle = \frac{3}{4}E_1^2E_2\cos(\phi)$ with a nontrivial quantum prefactor. At $T = 0$, the current response is not analytical in the driving amplitude. Unfortunately, in this case we do not find a simple approximate analytical expression for the current like the one in equation (129). Some numerical calculations [102], see also in figure 8, reveal a series of nontrivial features as the occurrence of current inversion and the occurrence of current maxima similar to the the case of stochastic dichotomous driving. Moreover, in the case of harmonic mixing driving the direction of the rectification current can be conveniently controlled by the phase ϕ. For a sufficiently large dissipation strength α, the rectification current response can also exhibit a Quantum Stochastic Resonance feature [188, 205–208, 216–218], i.e., it exhibits a maximum versus the temperature T. An experimental realisation of the dissipative quantum rectifiers in the studied incoherent tunnelling regime can be expected for the semiconductor superlattices [219] and for a small polaron like transport in molecular chains.

8. Summary

We have surveyed, extended and justified in great detail the results of recent research which relates to quantum dynamics with fluctuating parameters. The nature of those fluctuations, that usually stem from the influence of externally applied fields,

or intrinsic degrees of freedom, is either of stochastic or coherent deterministic origin. Our general findings are applied to specific situations, encompassing solid state applications, but mainly we did focus on the theme of driven ET in molecular aggregates.

A first major result is the derivation of the generalised non-Markovian master equations and the generalised Redfield equations for quantum systems composed of a finite, discrete number of states which are subject to the influence of external either stochastic, or periodic fields. The resulting kinetic equations allow one to study a rich variety of different physical problems within a unified framework. In the simplest cases, the relevant part of the reduced dynamics is either described by the Markovian balance equation of the Pauli master equation type [220] which is generalised to include the influence of explicit time-dependent, external field manipulations into the quantum transition rates; those becoming therefore functionals of the driving field, or by its generalisation which accounts as well for the memory effects in the corresponding dissipative kernels.

In the case of fast (on the time-scale of the averaged relaxation process) fluctuating, or oscillating fields these quantum kinetic equations can be averaged. The relaxation transitions can be described by the averaged quantum transition rates of the Golden Rule type. These averaged transition rates, however, generally do not satisfy the detailed balance condition at the temperature of the thermal bath. This violation of the thermal detailed balance, being induced by the *non-equilibrium* driving fields, in turn paves a roadway for identifying several intriguing nonequilibrium phenomena.

An important case is provided by symmetric dichotomous driving fields for which our approximate theories and considerations can be made rigorous, tested and reaffirmed [67, 100, 101] because the corresponding averaging can be performed exactly.

The problem of averaging a quantum dynamics in stochastic fields modelled by non-Markovian processes of the continuous time random walk type with a discrete number of states (with Markovian processes emerging as a particular limiting case) has been investigated in the absence of dissipation in section 2. Using a classical stochastic path integral approach, we obtained some general exact results on the averaging of quantum propagator of the driven quantum system over the *stationary* realisations of such non-Markovian jump processes. In particular, the exact result for the Laplace transform of the correspondingly averaged quantum propagator has been obtained. This novel result bears the potential for future applications since it opens a way for a rigorous study of an extreme case of $1/f^{\alpha}$ noise, implying long-range temporal correlations, where standard perturbation theory is expected to fail. As a first important application, we obtained the spectral line shape of the corresponding Kubo oscillator and the Laplace-transformed averaged evolution of a spin-1/2 system that is driven by a symmetric alternating renewal process possessing an arbitrary distribution of the residence times. This implies a very broad class of autocorrelation functions including those which correspond to noise sources with $1/f^{\alpha}$ power spectrum. This general result is shown to reproduce the known solution in the Markovian limit, i.e. when the the residence time intervals are exponentially distributed.

Starting out with section 4, we have investigated the combined effects of fluctuating parameters and dissipation on the evolution of the corresponding

quantum dynamics. In doing so, we considered both the role of fluctuations of the energy bias, and/or the effects of a fluctuating intersite tunnelling matrix element. A generalised master equation was obtained which corresponds to the known NIBA approximation obtained within the quantum path-integral approach. The obtained master equation was averaged exactly both over dichotomous fluctuations of the energy bias and dichotomous fluctuations of the tunnelling coupling, i.e. the case with a fluctuating tunnelling barrier. These results have been used to study a rich repertoire of nonequilibrium phenomena for ET in condensed media with dynamical disorder and possibly being driven by stochastic or deterministic, coherent periodic laser fields.

In section 7 we have studied the quantum transport in extended quantum systems within a tight-binding description, with the dynamics being subjected to a strong system-bath coupling and weak tunnelling, i.e. in the limit of an incoherent hopping regime. A general result for the quantum-noise assisted transport current, being averaged over the field fluctuations, has been derived. The corresponding expression is shown to be equivalent to the NIBA approximation result of a corresponding quantum path integral treatment.

Our theory for dissipative systems with fluctuating parameters predicts scores of interesting nonequilibrium phenomena that are the result of a stunning interplay between equilibrium quantum fluctuations and nonequilibrium perturbations. A few noteworthy such effects are: (i) the suppression, or acceleration of quantum transition rates by many orders of magnitude; (ii) a noise-induced enhancement of the thermally assisted quantum tunnelling; (iii) the inversion of populations in the spin-boson model; or (iv) a noise-induced absolute negative mobility in quantum transport. We further elaborated on the theme of dissipative quantum rectifiers. Several of these novel predictions are presently being investigated in a number of research groups, both theoretically and experimentally. Our research in particular also impacts such timely activities like the investigation of the electronic transport in infrared laser driven molecular wires [221]. Here, the fermionic thermal baths are provided by the electronic reservoirs in the leads and the electron transport through the wire is mainly coherent. This corresponds to the regime of a weak dissipation within our approach, being opposite to the regime of incoherent tunnelling. The role of the size, inter-electrode coupling effects, etc. [222] as well as the inelastic Coulomb repulsion effects [223], are also important for molecular wires. This brings about further complications that still need to be investigated theoretically with greater detail. Experimental progress is presently also forthcoming [224]: this particularly holds true for quantum Brownian motors and quantum rectifiers as witnessed by the exemplary set of recent experimental studies [225–230]. We share the confident belief that this research topic will remain flourishing and, moreover, will invigorate the readers in pursuing their own future research in this area.

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