Dynamics of Open Quantum Systems

Edited by

Keith H. Hughes

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School of Chemistry
University of Wales Bangor
Bangor
LL57 2UW
United Kingdom

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Preface

This booklet was produced as a result of the CCP6 Workshop on the "Dynamics of Open Quantum Systems" held at the University of Wales Bangor, UK, between August 22-25, 2006. The workshop was sponsored by the UK Collaborative Computation Project 6 (CCP6) on molceular quantum dynamics. Details of CCP6 and its activities can be found at http://www.ccp6.ac.uk. Although CCP6 was the main sponsor of this event the workshop also received support from Gaia Technologies.

The workshop was designed to bring together researchers from a range of disciplines that span the broad subject of dissipative quantum systems. New approaches and formulations of quantum dissipation theory were discussed along with a discussion of how dissipation affects key dynamical processes such as electron transfer and transport, surface dynamics, quantum control and non-adiabatic effects. Most of the speakers presentations are available for download from the workshop website
http://www.chemistry.bangor.ac.uk/khh/ccp6/index.htm

Each speaker was asked to provide a brief article which could be collected into a workshop booklet that reviews their work and the topics covered in their talk. This booklet should be of interest to both the specialist and non-specialist in this field. The booklet contains primers to the topic of dissipative quantum systems and should serve as a guide to many of the recent developments in this field. The editor would like to thank all those who participated and contributed to the workshop.

K. H. Hughes, Bangor
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Quantum Dissipation: A Primer

Peter Hänggi[(a), (b)]
(a) Universität Augsburg, Department of Physics,
Universitätsstr. 1, 86135 Augsburg, Germany
(b) National University of Singapore,
Faculty of Science, Physics Department, Blk S12,
2 Science Drive 3, 117542 Singapore, Singapore

I. INTRODUCTION

Albert Einstein explained the phenomenon of dissipation and Brownian motion in his *annus mirabilis* of 1905 by use of statistical methods which he ingeniously combined with the laws of thermodynamics. In this pioneering work he as well provided a first link between the dissipative forces and the impeding thermal fluctuations, known as the *Einstein relation* which relates the strength of diffusion to the friction. This intimate connection between dissipation and related fluctuations was put on a firm basis much later when Nyquist and Johnson considered the spectral density of voltage- and current-fluctuations.

What role do quantum mechanics and the associated quantum fluctuations play in this context? After the birth of quantum mechanics in the early 1920's we can encounter in the very final paragraph of the 1928 paper by Nyquist for the first time the introduction of quantum mechanical noise via the substitution of the energy kT from the classical equipartition law by the thermally averaged quantum energy (but leaving out the zero point energy contribution) of the harmonic oscillator. Nyquist's remark thus constitutes a precursor of the celebrated work by Callen and Welton who generalized the relations by Einstein, Nyquist and Johnson to include quantum effects.

Without doubt, quantum fluctuations constitute a prominent noise source in many nano-scale and biological systems. Let me just mention one situation here: the tunnelling and the transfer of electrons, quasi-particles, and alike, is assisted by noise for which the quantum nature *cannot* be neglected. The features of this noise change drastically as a function of temperature: at sufficiently high temperatures a crossover occurs to classical Johnson-Nyquist (thermal) noise.

There exist a rich variety of methods to tackle quantum fluctuations and quantum dissipation in open systems in particular. I mention here the generalized quantum master equation (QME) approach, the quantum Langevin description (QLE), the powerful functional integral techniques for the time evolution for a corresponding reduced density operator, the stochastic Liouville-von Neumann equations, stochastic and nonlinear Schrödinger equations, the method of quantum trajectories, etc.. Some of these schemes are *formally* equivalent – others are not. Rather than presenting in this report only a glimpse of such methods taken from this rich zoo of differing approaches to quantum dissipation I decided to focus in some greater detail on one such approach: the formalism of a – *Quantum Langevin Equation* –, together with a discussion of subtleties and possible shortcomings. This QLE is capable of describing consistently quantum friction within a quantum mechanical setting. At the end I will list some sources dealing with the description of open, dissipative quantum systems for useful further reading.

II. DISSIPATION IN NONLINEAR QUANTUM SYSTEMS: THE GENERALIZED QUANTUM LANGEVIN EQUATION (QLE)

A. Bath of oscillators

A popular model for the dynamics of a dissipative quantum system subject to quantum Brownian noise is obtained by coupling the system of interest to a bath of harmonic oscillators. Accordingly, we write for the total Hamiltonian

$$\begin{aligned} H = {} & \frac{p^2}{2M} + V(q,t) \\ & + \sum_{i=1}^{N} \left[\frac{p_i^2}{2m_i} + \frac{m_i}{2}\omega_i^2 x_i^2 - q c_i x_i + q^2 \frac{c_i^2}{2m_i\omega_i^2} \right] \end{aligned} \tag{1}$$

where the first two terms describe the system as a particle of mass M moving in a generally time-dependent potential $V(q,t)$. The sum contains the Hamiltonian for a set of N harmonic oscillators which are *bi-linearly* coupled with strength c_i to the system. Finally, the last term, which depends only on the system coordinate, represents a potential renormalization term which is needed to ensure that $V(q,t)$ remains the bare potential. This Hamiltonian has been studied since the early 60's for systems which are weakly coupled to the environmental degrees of freedom. Only after 1980, it was realized by Caldeira and Leggett that this model is also applicable to strongly damped systems and may be employed to describe, for example, dissipative tunnelling in solid state physics and chemical physics.

B. Quantum Langevin equation

One may convince oneself that the Hamiltonian (1) indeed models dissipation. Making use of the solution of the Heisenberg equations of motion for the external degrees of freedom one derives a reduced system operator equation of motion, the so-called *generalized quantum Langevin equation (QLE)*

$$M\ddot{q}(t) + M\int_{t_0}^{t} ds\gamma(t-s)\dot{q}(s) + \frac{dV(q,t)}{dq} = \xi(t) \qquad (2)$$

with the damping kernel

$$\gamma(t) = \gamma(-t) = \frac{1}{M}\sum_{i=1}^{N}\frac{c_i^2}{m_i\omega_i^2}\cos(\omega_i t) \qquad (3)$$

and the quantum Brownian force operator

$$\begin{aligned}\xi(t) = &-M\gamma(t-t_0)q(t_0)\\ &+\sum_{i=1}^{N} c_i\Bigg(x_i(t_0)\cos(\omega_i[t-t_0])\\ &\qquad + \frac{p_i(t_0)}{m_i\omega_i}\sin(\omega_i[t-t_0])\Bigg)\,.\end{aligned} \qquad (4)$$

The generalized quantum Langevin equation (2) appears first in a paper by Magalinskiĭ who started from (1) in the absence of the potential renormalization term.

The force operator (4) depends explicitly on the initial conditions at time t_0 of the bath position operators $x_i(t_0)$ and bath momenta $p_i(t_0)$. The initial preparation of the total system, which fixes the statistical properties of the bath operators and the system degrees of freeedom, turns the force $\xi(t)$ into a random operator. Note that this operator depends not only on the bath properties but as well on the initial system position $q(t_0)$. To fully specify the reduced dynamics it is thus of importance to specify the preparation procedure. This in turn then also fixes the statistical properties of the quantum Brownian noise. Clearly, in order to qualify as a stochastic force the random force $\xi(t)$ should not be biased; i.e. its average should be zero at all times. Moreover, this Brownian quantum noise should constitute a *stationary* process with time homogeneous correlations.

Let us also introduce next the auxiliary random force $\eta(t)$, defined by

$$\eta(t) = \xi(t) + M\gamma(t-t_0)q(t_0) \qquad (5)$$

which only involves bath operators. In terms of this new random force the QLE (2) no longer assumes the form of an ordinary generalized Langevin equation: it now contains an inhomogeneous term $\gamma(t-t_0)q(t_0)$, the initial slip term. This term is often neglected in the so-called "Markovian limit" when the friction kernel assumes the ohmic form $\gamma(t) \to 2\gamma\delta(t)$. For a correlation-free preparation, the initial total density matrix is given by the product $\rho_T = \rho_S(t_0)\rho_{\text{bath}}$, where $\rho_S(t_0)$ is the initial system density matrix. The density matrix of the bath alone assumes canonical equilibrium, i.e.

$$\rho_{\text{bath}} = \frac{1}{\mathcal{N}} \exp\left(-\beta \sum_{i=1}^{N} \left[\frac{p_i^2}{2m_i} + \frac{m_i}{2}\omega_i^2 x_i^2 \right] \right) , \tag{6}$$

with $\mathcal{N}$ denoting a normalization constant.

The statistical properties of the random force $\eta(t)$ then follow immediately: $\eta(t)$ is a stationary *Gaussian operator noise* obeying

$$<\eta(t)>_{\rho_{\text{bath}}} = 0 \tag{7}$$

$$\begin{aligned} S_{\eta\eta}(t-s) &= \frac{1}{2} <\eta(t)\eta(s) + \eta(s)\eta(t)>_{\rho_{\text{bath}}} \\ &= \frac{\hbar}{2} \sum_{i=1}^{N} \frac{c_i^2}{m_i\omega_i} \cos\big(\omega_i(t-s)\big) \coth\left(\frac{\hbar\omega_i}{2kT}\right) . \end{aligned} \tag{8}$$

Being an operator-valued noise, its commutator does not vanish

$$[\eta(t), \eta(s)] = -i\hbar \sum_{i=1}^{N} \frac{c_i^2}{m_i\omega_i} \sin\big(\omega_i(t-s)\big) . \tag{9}$$

Setting for the initial position operator $q(t_0) = q_0$, the last expression in (8) is also valid for the noise correlation $S_{\xi\xi}(t)$ of the noise force $\xi(t)$ provided the average is now taken with respect to a bath density matrix which contains shifted oscillators. The initial preparation of the bath is then given by the new density matrix $\hat{\rho}_{\text{bath}}$;

$$\begin{aligned} \hat{\rho}_{\text{bath}} = \frac{1}{\mathcal{N}} \exp\Big\{ -\beta \Big[\sum_i \frac{p_i^2}{2m_i} \\ + \frac{m_i\omega_i^2}{2} \left(x_i - \frac{c_i}{m_i\omega_i^2}\, q_0 \right)^2 \Big] \Big\} . \end{aligned} \tag{10}$$

This scheme of the QLE can also be extended to the nonequilibrium case with the system attached to two baths of different temperature. Two most recent applications address the problem of the thermal conductance through molecular wires that are coupled to leads of different temperature. Then the heat current assumes a form similar to the Landauer formula for electronic transport: The heat current is given in terms of a transmission factor times the difference of corresponding Bose functions.

Furthermore, the QLE concept can be extended as well to *fermionic* systems which are coupled to electron reservoirs and which, in addition, may be exposed to time-dependent driving. The corresponding Gaussian quantum noise is now composed of fermion annihilation operators.

C. Important subtleties and pitfalls

The use of the generally nonlinear QLE (2) is limited in practice for several reasons. More importantly, the application of the QLE bears some subtleties and pitfalls which must be observed when making approximations. These same subtleties typically also emerge with other approaches/methods to quantum dissipation; thus it is beneficial to dwell on these in some detail. Important features of the QLE are:

- The QLE (2) is an operator equation that acts in the full Hilbert space of system and bath. The coupling between system and environment also implies an entanglement upon time evolution even for the case of an initially factorizing full density matrix. Together with the commutator property of quantum Brownian motion, see eq. (9), we find that the reduced, dissipative dynamics of the position operator $q(t)$ and momentum operator $p(t)$ obey – as they should – the Heisenberg uncertainty relation for *all times*.

This latter feature is crucial. For example, the non-Markovian (colored) Gaussian quantum noise with real-valued correlation $S_{\xi\xi}(t) = S_{\xi\xi}(-t)$ cannot simply be substituted by a *classical* non-Markovian Gaussian noise force which identically obeys the correlation properties of (Gaussian) quantum noise $\xi(t)$. An approximation of this type clearly would not satisfy the commutator property for position and conjugate momentum of the system degrees of freedom.

The literature is full of various such attempts wherein one approximates the quantum features by corresponding colored classical noise sources. Such schemes work at best near a quasi-classical limit, but even then care must be exercised. For example, for problems that exhibit an exponential sensitivity, such as the dissipative decay of a meta-stable state discussed in the next section, such an approach gives no exact agreement with the quantum dissipative theory. It is only in the classical high temperature limit, where the commutator structure of quantum mechanics no longer influences the result. Perfect agreement is only achieved in the classical limit.

The study of quantum friction in a nonlinear quantum system by means of the QLE (2) is plagued by the fact that the nonlinearity forbids an explicit solution. This solution, however, is needed to obtain the statistical properties such as mean values and correlation functions. This (unknown) nonlinear response function also determines the derivation of the rate of change of the reduced density operator, i.e. the generalized quantum master equation (QME), and its solution of the open quantum system.

The very fact that the QLE acts in *full* Hilbert space of system and environment also needs to be distinguished from the classical case of a generalized Langevin equation. There, the stochastic dynamics acts solely on the state space of the system dynamics with the (classical) noise properties specified a priori.

- The quantum noise correlations can, despite the explicit microscopic expression given in (8), be expressed solely by the macroscopic friction kernel $\gamma(t)$.

This result follows upon noting that the Laplace transform $\hat{\gamma}(z)$ of the macroscopic friction assumes with $\mathrm{Re} z > 0$ the form

$$\hat{\gamma}(z) = \frac{1}{2M} \sum_{i=1}^{N} \frac{c_i^2}{m_i \omega_i^2} \left[\frac{1}{z - i\omega_i} + \frac{1}{z + i\omega_i} \right] . \tag{11}$$

With help of the well known relation $1/(x + i0^+) = P(1/x) - i\pi\delta(x)$ we find that

$$\begin{aligned} &\mathrm{Re}\hat{\gamma}(z = -i\omega + 0^+) \\ &\qquad = \frac{\pi}{2M} \sum_{i=1}^{N} \frac{c_i^2}{m_i \omega_i^2} \left[\delta(\omega - \omega_i) + \delta(\omega + \omega_i) \right] . \end{aligned} \tag{12}$$

By means of (8) we then find the useful relation

$$\begin{aligned} S_{\xi\xi}(t) &= S_{\eta\eta}(t) \\ &= \frac{M}{\pi} \int_0^\infty d\omega \mathrm{Re}\hat{\gamma}(-i\omega + 0^+) \hbar\omega \coth\left(\frac{\hbar\omega}{2kT} \right) \cos(\omega t) . \end{aligned} \tag{13}$$

In the classical limit this relation reduces, independent of the preparation of the bath with ρ or $\hat{\rho}$, to the non-Markovian Einstein relation $S_{\xi\xi}(t) = MkT\gamma(t)$. The relation (13) is by no means obvious: It implies that a modelling of quantum dissipation is possible in terms of macroscopic quantities such as the friction kernel $\gamma(t)$ and the temperature T. For other coupling schemes between system and bath we generally can no longer express the correlation of quantum noise exclusively in terms of macroscopic transport coefficients. As an example we mention the coupling of the system to a bath of two-level systems (spin bath) rather than to a bath of harmonic oscillators.

Note also the following differences to the classical situation of a generalized Langevin equation.

- The quantum noise $\xi(t)$ is correlated with the initial position operator $q(t_0)$. This feature that $<q(t_0)\xi(t)>_{\hat{\rho}} \neq 0$ follows from the explicit form of the quantum noise $\xi(t)$. The correlation function vanishes only in the classical limit. Note also that the expectation value of the system-bath interaction is finite at zero temperature. These features reflect the fact that at absolute zero temperature the coupling induces a non-vanishing decoherence via the zero-point fluctuations.

Moreover,

- the initial slip term $\gamma(t-t_0)q(t_0)$ appears also in the absence of the potential renormalization in the Hamiltonian (1). With this initial value contribution being absorbed into the quantum fluctuation $\xi(t)$, these become stationary fluctuations with respect to the initial density operator of the bath $\hat{\rho}_{\mathrm{b}ath}$ given by (10). Note, however, that with respect to an average over the bare, non-shifted bath density operator $\rho_{\mathrm{b}ath}$, the quantum fluctuations $\xi(t)$ would become non-stationary.

It is also worthwhile to point out here that this initial value term in the QLE should not be confused with the initial value term that enters the corresponding generalized QME. In the case of a classical reduced dynamics it is always possible – by use of a corresponding projection operator – to formally eliminate this initial, inhomogeneous contribution in the generalized master equation. This in turn renders the time evolution of the reduced probability a truly linear dynamics. This property no longer holds for the reduced quantum dynamics: for a non-factorizing initial preparation of system and bath this initial value contribution in the QME generally is finite and presents a *true nonlinearity* for the time evolution law of the open quantum dynamics.

There exist even further subtleties which are worthwhile to point out. The friction enters formally the QLE just in the same way as in the classical generalized Langevin equation. In particular, a time-dependent potential $V(q,t)$ leaves this friction kernel invariant in the QLE. In contrast to the classical Markovian case, however, where the friction enters the corresponding Fokker-Planck dynamics independent of the time scale of driving, this is no longer valid for the generalized quantum master equation dynamics of the corresponding reduced density matrix.

For the bilinear system-bath interaction with the bath composed of harmonic oscillators it was possible to integrate out the degrees of freedom of the bath explicitly. Does this hold as well for other interactions? The elimination of the bath degrees of freedom is still possible for a nonlinear coupling to a bath of harmonic oscillators if the system part of the coupling is replaced by a nonlinear operator-valued function of either the momentum or position degree of freedom of the system as long as the bath degrees of freedom appear linearly. The resulting friction kernel then appears as a nonlinear friction but the influence of the bath degrees of freedom is still obtained in exact form.

Yet another situation for which one can derive an exact QLE is when a nonlinear system, such as a spin degree of freedom, interacts with a collection of quantum (Bose) oscillators in such a way that the interaction Hamiltonian *commutes* with the system Hamiltonian, thus constituting a quantum non-demolition interaction. This case corresponds to pure dephasing; it was originally addressed by Łuczka and van Kampen for the problem of a spin in contact with a thermal heat bath.

We end this subsection by mentioning also the coupling of a system to a bath of independent fermions with infinitely many excitation energies: a suitable transformation then allows a mapping of the dissipation onto a bosonic environment with an appropriate coupling strength.

III. FURTHER READING

The presented material outlined above is based on a longer comprehensive article which I co-authored with Prof. Dr. G.-L. Ingold. It appeared during the world year of physics in 2006 in the journal *CHAOS* (see below) in celebration of Einstein's work of 1905 on Brownian motion. The reader can find further insightful information on the use and abuse of *quantum dissipation* by consulting the pdf's of recent review and feature articles on the web: **http://www.physik.uni-augsburg.de/theo1/hanggi/Quantum.html**

Some useful such reports for further reading are:

- T. Dittrich, P. Hänggi. G.-L. Ingold, B. Kramer, G. Schön, and W. Zwerger, *Quantum Transport and Dissipation* (Wiley-VCH, Weinheim, 1998).
- M. Grifoni and P. Hänggi, *Driven Quantum Tunneling*, Phys. Rep. **304**: 229-354 (1998)
- U. Weiss, *Quantum Dissipative Systems*, second edition (World Scientific, Singapore, 1999)
- G.-L. Ingold, *Path integrals and their application to dissipative quantum systems*, Lect. Notes Phys. **611**: 1-53 (2002)
- S. Kohler, J. Lehmann, and P. Hänggi, *Driven quantum transport on the nanoscale*, Phys. Rep. **406**: 379-443 (2005)
- I. Goychuk and P. Hänggi *Quantum dynamics in strong fluctuating fields*, Adv. Physics. **54**: 525-584 (2005)
- P. Hänggi and G. L. Ingold, *Fundamental aspects of quantum Brownian motion*, Chaos **15**: 026105 (2005)

The above link also provides access to the pdf of the talk which I presented for CCP6, Dynamics of Open Quantum systems, at the University of Wales, Bangor, August 23-25, 2006.