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Friction and noise in quantum mechanics: A model for the interactions between a system and a thermal bath(*)

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Summary. — The time evolution equation of the *reduced* density matrix of a quantum system composed of one or many particles subjected to a conservative force field and interacting with a thermal bath has been derived. This result is achieved by analogy with classical models based upon the Langevin and Fokker-Planck equations. According to the Langevin approach, the interaction is modelled by means of a random force field and a viscous friction term. We generalise this classical approach introducing suitable operators that describe the quantum evolution of a system weakly coupled to a thermal bath. In particular, we define a kind of friction operator that can be thought as the quantal counterpart of the classical Langevin term corresponding to the viscous force. The proposed approach has the invaluable advantage of yielding a handy differential equation to model the quantum interaction between a system and a thermal bath.

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1. – Introduction

The behaviour of a microscopic physical system during its time evolution is of general interest in many fields ranging from theoretical physics to advanced technology and biology. Various attempts to analyse the coherent and incoherent evolution of the system

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(**) Alessandro Chiabrera, born 1940, died in 1999. The other co-authors wish to dedicate this paper to His beloved memory.

due to the coupling with the external thermal bath have been developed in the fields of magnetic resonance [1, 2], atomic excitation [3], laser [4, 5], as long as in molecular electronics [6], quantum computing [7, 8], and bioelectromagnetics [9, 10]. Thus, it is a common problem of many disciplines to analyse quantum systems driven away from thermal equilibrium. The most useful tool for handling the quantum thermal relaxation is the *reduced* density matrix [11], because it allows the introduction of *mixed* states describing a system coupled to a thermal bath as functions of the system state variables only. The evolution equation concerning the density matrix of a physical system in thermal contact with a reservoir, the so-called Generalised Master Equation (GME), can be found in literature [12, 13]. This topic has already been covered by many authors and from many points of view. Following a well-known procedure introduced by Levi-Civita (1896), Caldirola gives a detailed model for the analysis of the nonconservative quantum systems, leading to the so-called Caldirola-Kanai equation [14,15]. An alternative method to derive quantum kinetic equations utilises the Feynman-Vernon forward-backward path integral; this approach has been adopted by Caldeira and Leggett [16] and more recently used by different authors [17,18]. In the present work, we propose an explicit time evolution equation for the *reduced* density matrix, which will enable us to make all the physical prediction about measurements bearing only on the particle system. It is obtained by tracing out the environment state variables in the *global* density matrix that describes as a single *global* system the system of particle under consideration together with the atoms which generate the force field acting on the particles and with the reservoir. Therefore, the *reduced* density matrix describes the thermal relaxation of a system, that we assume to be composed by one or more particles, subjected to a conservative time-invariant force field and embedded in a thermal bath. This seems to be a plausible approach to handle the complexity of the interaction of a system with a reservoir. The thermal coupling, *i.e.*, energy and momentum transfers with the reservoir, is accounted for by introducing white Gaussian noise to emulate the *direct* interactions with particles, and viscous drag to emulate *indirect* interactions. This goal is achieved by analogy with classical models based upon the Fokker-Planck equation [19] associated to the Langevin equation. Our final differential equation is shown to be fully compatible with GME and thus it leads to the same kind of time evolution. The comparison with the above-mentioned results [12] clarifies that while the GME is useful, in principle, for a wide range of applications, it does not provide a closed form expression for its characteristic parameters. Conversely, in our approach a plausible and explicit model for the interaction is adopted, in such a way that a closed form expression for the quantum relaxation parameters, as functions of the classical ones, *i.e.* collision frequency and diffusion coefficient, can be found in closed form.

2. – Classical noise and friction

As an introduction to the sections devoted to quantum-mechanical considerations, let us review some classical well-known results, related to a set of N identical particles considered as material points. Let m be their mass and q_i, p_i $(i = 1, \ldots, 3N)$ their canonical coordinates and conjugate momenta, respectively. We assume that the reference frame is Cartesian, so that the q_i's actually are the values of the Cartesian coordinates x, y, z of the N particles and the p_i's are their momentum components.

Let us suppose, furthermore, that the N material points are subjected to a potential energy $U(q_1, q_2, \ldots, q_{3N})$ and that they are in contact with a thermal bath. This latter can be thought as a large ensemble of other particles, or more complex subsystems, which interact with the given N particles. With the above assumptions, the interaction can

be modelled by two kinds of forces according to the classical Langevin scheme: viscous friction and white Gaussian noise. It turns out that Gaussian noise forces describe the *direct* interaction of each particle of the ensemble of N particles, composing the system under consideration, with the surrounding particles (or subsystems) composing the thermal bath. Conversely, friction is responsible for the energy loss of the system due to transfer of momentum from its N particles and those belonging to the thermal bath, from the closest ones to the system to the farther away ones (*indirect* interaction).

The time evolution of the system of N particles can be obtained, in a classical mechanics scheme, from the well-known Langevin set of generalised Hamiltonian equations

$$\begin{cases} \dot{q}_k = \dfrac{p_k}{m}, \\ \dot{p}_k = -\dfrac{\partial U}{\partial q_k} - \beta p_k + \sqrt{D}\, m n_k(t), \end{cases} \tag{1}$$

where β is a viscous friction coefficient, D is the diffusion constant and each n_k is a white-noise term. The ensemble properties of noise are described by the expectation values below

$$E\{n_k(t)\} = 0, \tag{2}$$

$$E\{n_j(t_1) n_k(t_2)\} = 2\delta_{jk}\delta(t_1 - t_2). \tag{3}$$

The term $\sqrt{D} m n_k(t)$ is the component of the noise force along the k-th coordinate; more precisely we have $q_1 = x_1$, $q_2 = y_1$, $q_3 = z_1$, $q_4 = x_2$, $q_5 = y_2$, $q_6 = z_2$ and so on; this means that if $s = 1, 2, 3$ and $u = 1, \ldots, N$, we have that $k = 3(u-1)+s$ is the component along the s-axis (x, y, z for $s = 1, 2, 3$, respectively) of the particle u.

The canonical coordinates in this case assume the character of stochastic processes because of the very presence of the noise. Therefore, it is plausible to describe the system evolution by means of the Fokker-Planck equation for the probability density in the phase space $W(q, p, t)$ [19]

$$\frac{\partial W}{\partial t} = \sum_{i=1}^{3N} \left\{ \frac{\partial U}{\partial q_i}\frac{\partial W}{\partial p_i} - \frac{p_i}{m}\frac{\partial W}{\partial q_i} + \beta W + \beta p_i \frac{\partial W}{\partial p_i} + D m^2 \frac{\partial^2 W}{\partial p_i^2} \right\}, \tag{4}$$

or, introducing the Poisson brackets,

$$\frac{\partial W}{\partial t} = \big\{H_0, W\big\} + \beta \sum_{i=1}^{3N} \big\{q_i, p_i W\big\} + D m^2 \sum_{i=1}^{3N} \big\{q_i, \{q_i, W\}\big\}, \tag{5}$$

where

$$H_0 = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U\big(q_1, q_2, \ldots, q_{3N}\big) \tag{6}$$

is the system Hamiltonian in the absence of interaction with the thermal bath.

On the right-hand side of eq. (5) it is easy to identify, respectively, the Liouville term, responsible for the evolution of the isolated system and the friction and noise terms.

Equation (5) above admits the stationary asymptotic solution (or, otherwise stated, has the solution for $t \to \infty$) given by

$$W_{\mathrm{eq}}(p,q) = \frac{\exp[-(\beta/mD)H_0]}{\iint_{\mathcal{R}^{6N}} \exp[-(\beta/mD)H_0]\mathrm{d}q\,\mathrm{d}p}, \tag{7}$$

where $\mathcal{R}^{6N}$ stands for the whole $6N$-dimensional phase space.

If we introduce the temperature T of the thermal bath, by means of the Einstein relationship [19]

$$K_{\mathrm{B}}T = \frac{Dm}{\beta}, \tag{8}$$

where K_{B} is the Boltzmann constant, eq. (7) becomes the well-known Boltzmann distribution

$$W_{\mathrm{eq}}(p,q) = \frac{1}{Z}\exp\left[-\frac{1}{K_{\mathrm{B}}T}H_0\right], \tag{9}$$

where Z is the classical partition function

$$Z = \iint_{\mathcal{R}^{6N}} \exp\left[-\frac{1}{K_{\mathrm{B}}T}H_0\right]\mathrm{d}q\,\mathrm{d}p. \tag{10}$$

3. – Quantum noise

If we do not consider the friction term in eq. (5) we obtain the following equation:

$$\frac{\partial W}{\partial t} = \{H_0, W\} + Dm^2\sum_{i=1}^{3N}\{q_i, \{q_i, W\}\}, \tag{11}$$

which classically describes a system perturbed by noise forces.

Now, we aim to find out the quantum equivalent of eq. (11); in order to do this, we firstly introduce in the Hamiltonian an effective potential energy which mimics the noise forces, according to the technique used by Abragam [1], in such a way as to obtain a formal Hamiltonian accounting for interaction with the thermal bath

$$H = H_0 + \sum_{i=1}^{3N}\sqrt{D}mq_in_i(t). \tag{12}$$

In quantum dynamics, the time evolution of a system can be described by the statistical operator ρ, which fulfils the well-known Liouville-Von Neumann equation

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{1}{i\hbar}[H, \rho]. \tag{13}$$

More precisely, this equation holds for *closed* systems. In order to deal with the system interacting with the thermal bath, we adopt [1] eq. (13) with the Hamiltonian given

by eq. (12). This amounts to formally handle the system as a closed one, taking into account that its true characteristic to be actually *open* is emulated by means of the "noisy" potential energy. From eqs. (12) and (13) it follows that

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{1}{i\hbar}[H_0, \rho] + \frac{\sqrt{D}m}{i\hbar}\sum_{i=1}^{3N}[q_i, \rho]n_i(t). \tag{14}$$

This is a Langevin-type, stochastic differential equation involving operators. It can be handled as an ordinary differential system involving *functions* once one chooses the well-known *superoperator* technique, in which conventional operators are represented as vectors in an operator space whilst commutators, since they act as linear operators in such a space, are referred to as superoperators. So doing, eq. (14) above can be recast into the following mathematical form:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = A\rho + \sum_i n_i(t)(B_i\rho) = \Big[A + \sum_i n_i(t)B_i\Big]\rho, \tag{15}$$

where now ρ is interpreted as a *vector* in the operator space, A is the linear superoperator corresponding to the commutator $(1/i\hbar)[H_0, \bullet]$ and B is another superoperator, corresponding to $(\sqrt{D}m/i\hbar)[q_k, \bullet]$. Moreover, one can represent the operator space through a suitable orthonormal basis, so that in eq. (15) ρ can be interpreted as a column vector and A, B as matrices. This double way of interpreting ρ, either as an operator or as a vector, is rather useful.

If we consider ρ as a vector, then eq. (15) is again an ordinary vector differential stochastic equation containing multiplicative noise. Its analysis can again be accomplished by means of an appropriate Fokker-Planck equation [19].

Now, the true reduced density matrix (or vector, as above said) of interest is not actually this ρ *per se*: clearly, what is relevant, for a description of the interaction of the N-particle system with the thermal bath, *is the average or expectation value* of this reduced density, needed to smooth the fluctuations due to noise.

The following fundamental theorem can be proved (see appendix): the evolution equation for *the expectation value* of $\rho = \rho(t)$ in eq. (15) with Gaussian noise fulfilling eqs. (2) and (3), is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}E\{\rho(t)\} = \Big[A(t) + \sum_i \big[B_i(t)\big]^2\Big]E\{\rho(t)\}. \tag{16}$$

Applying this theorem to eq. (14) it is easy to obtain the equation for the expectation value of ρ, *i.e.* $E\{\rho\}$:

$$\frac{\mathrm{d}}{\mathrm{d}t}E\{\rho\} = \frac{1}{i\hbar}\big[H_0, E\{\rho\}\big] - \frac{m^2 D}{\hbar^2}\sum_{i=1}^{3N}\big[q_i, \big[q_i, E\{\rho\}\big]\big]\,. \tag{17}$$

Doing the formal substitution $\{\bullet, \bullet\} \to (1/j\hbar)[\bullet, \bullet]$ described, for instance, by Messiah [20] and Schiff [21], this relationship becomes strictly analogous to eq. (11).

We wish to put in evidence the fact that eq. (17) has been obtained on a rigorous basis and that the analogy with eq. (11) has been made just to enforce the validity and understanding of our result.

Besides, it is worthwhile to point out an intrinsic limitation of this model: it has been developed by using white noise, thus completely uncorrelated. This is just an approximation equivalent to the Markovian process hypothesis for the thermal interaction process. A better model should take into account noise forces with finite correlation time. The above-discussed approximation is, however, considered satisfactory for the pourpose of this work.

4. – Quantum friction

Now we deal with the problem of finding a suitable quantum analogous for the friction term in eq. (5). The addition of such a contribution in eq. (17) is unavoidable also because in that equation $E\{\rho\}$, per se, does not evolve to any asymptotic distribution while it should evolve toward thermodynamic equilibrium value $E\{\rho_{\mathrm{eq}}\}$. Without the friction term, the mean energy would grow linearly with respect to the time variable, its time derivative being Dm. Therefore, we further exploit the analogy: the commutators substitute the Poisson brackets, a factor $1/i\hbar$ apart. Unfortunately no strict analogous is known for the product $p_k W$. On the other hand, we can assume that a possible and plausible choice is a symmetrized term of the form $1/2(\Theta_k E\{\rho\} + E\{\rho\}\Theta_k)$, where Θ_k are some suitable Hermitian operators that should play the role of p_k in the analogy. Under these assumptions the complete final form of eq. (5) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}E\{\rho\} = \frac{1}{i\hbar}\big[H_0, E\{\rho\}\big] + \frac{\beta}{2i\hbar}\sum_{i=1}^{3N}\big[q_i, \Theta_i E\{\rho\} + E\{\rho\}\Theta_i\big] - \frac{Dm^2}{\hbar^2}\sum_{i=1}^{3N}\big[q_i, \big[q_i, E\{\rho\}\big]\big]. \tag{18}$$

A suitable Θ_k operator must fulfil the following physical constraints:

– It must be Hermitian in order to guarantee the hermiticity of the reduced density matrix.

– It must lead to an asymptotic state described by the quantum Boltzmann distribution

$$E\{\rho_{\mathrm{eq}}\} = \frac{1}{Z}\exp\left[-\frac{1}{K_{\mathrm{B}}T}H_0\right], \tag{19}$$

where Z is the quantum partition function

$$Z = \mathrm{Tr}\left\{\exp\left[-\frac{1}{K_{\mathrm{B}}T}H_0\right]\right\}. \tag{20}$$

– It must be in some way strictly analogous to the linear momentum p_k, and possibly it must become coincident with p_k in same specific conditions.

Thus, fulfilling the asymptotic behaviour given by eq. (17), we obtain the following constraint:

$$\Theta_k e^{-(H_0/K_{\mathrm{B}}T)} + e^{-(H_0/K_{\mathrm{B}}T)}\Theta_k = \frac{2mK_{\mathrm{B}}T}{\hbar} i\big[q_k, e^{-(H_0/K_{\mathrm{B}}T)}\big], \quad \forall k. \tag{21}$$

Actually, this is a kind of a Lyapunov equation [22], in the unknown Θ_k, whose solution, as one easily verifies, is

$$\Theta_k = \frac{2mK_{\mathrm{B}}T}{\hbar} i \int_0^{+\infty} \exp\big[-\xi e^{-(H_0/K_{\mathrm{B}}T)}\big]\big[q_k, e^{-(H_0/K_{\mathrm{B}}T)}\big] \exp\big[-\xi e^{-(H_0/K_{\mathrm{B}}T)}\big] \mathrm{d}\xi. \tag{22}$$

This is the first integral form for the quantum friction operators.

A possible way to show how close is this operator to p_k is to derive another expression as follows. Let us introduce the Heisenberg picture $\tilde{O}$ for any operator corresponding to the time-independent operator O in the Schroedinger picture. Therefore letting

$$\begin{cases} \tilde{\Theta}_k = e^{+i(H_0/\hbar)t} \Theta_k e^{-i(H_0/\hbar)t}, \\ \tilde{p}_k e^{+i(H_0/\hbar)t} p_k e^{-i(H_0/\hbar)t}, \end{cases} \tag{23}$$

in the Heisenberg picture eq. (21) becomes

$$\tilde{\Theta}_k + e^{-(H_0/K_{\mathrm{B}}T)} \tilde{\Theta}_k e^{+(H_0/K_{\mathrm{B}}T)} = \frac{2mK_{\mathrm{B}}T}{\hbar} i\big(\tilde{q}_k - e^{-(H_0/K_{\mathrm{B}}T)} \tilde{q}_k e^{+(H_0/K_{\mathrm{B}}T)}\big). \tag{24}$$

Recalling the well-known identity, which holds true for any couple of operators A, Q,

$$e^{At} Q e^{At} = Q + [A, Q] + \frac{1}{2!}\big[A, [A, Q]\big] + \cdots, \tag{25}$$

we apply it to the two terms with exponentials appearing in eq. (24). Then, eq. (24) becomes

$$\begin{aligned} &\tilde{\Theta}_k + \tilde{\Theta}_k + \left[-\frac{H_0}{K_{\mathrm{B}}T}, \tilde{\Theta}_k\right] + \frac{1}{2!}\left[-\frac{H_0}{K_{\mathrm{B}}T}, \left[-\frac{H_0}{K_{\mathrm{B}}T}, \tilde{\Theta}_k\right]\right] + \cdots = \\ &\quad = \frac{2mK_{\mathrm{B}}T}{\hbar} i\left(\tilde{q}_k - \tilde{q}_k + \left[-\frac{H_0}{K_{\mathrm{B}}T}, \tilde{q}_k\right] - \frac{1}{2!}\left[-\frac{H_0}{K_{\mathrm{B}}T}, \left[-\frac{H_0}{K_{\mathrm{B}}T}, \tilde{q}_k\right]\right] + \cdots\right). \end{aligned} \tag{26}$$

For any linear time-independent operator $\tilde{O}$ in Heisenberg picture, the following equation holds true:

$$\left[-\frac{H_0}{K_{\mathrm{B}}T}, \tilde{O}\right] = \frac{i\hbar}{K_{\mathrm{B}}T} \frac{\mathrm{d}\tilde{O}}{\mathrm{d}t}. \tag{27}$$

When this rule is applied to eq. (26), letting $\tilde{O} = \tilde{\Theta}_k$, in the left-hand side and $\tilde{O} = \tilde{q}_k$ on the right-hand side, one identifies the Taylor series expansions of $\tilde{\Theta}_k$ and $\tilde{q}_k$ with respect to time, in such a way that eq. (26) becomes

$$\tilde{\Theta}_k(t) + \tilde{\Theta}_k\left(t + \frac{i\hbar}{K_{\mathrm{B}}T}\right) = \frac{2mK_{\mathrm{B}}T}{\hbar} i\left[\tilde{q}_k(t) - \tilde{q}_k\left(t + \frac{i\hbar}{K_{\mathrm{B}}T}\right)\right]. \tag{28}$$

It must be noticed that in the present form the operators involved in eq. (28) have either real or complex arguments: this is an *analytic continuation* from real to complex time.

Equation (28) can be easily handled, if one uses Fourier transform (with respect to time).

So doing, we obtain

$$\tilde{\theta}_k(\Omega) = \frac{2mK_{\mathrm{B}}T}{\hbar} i\tilde{Q}_k(\Omega)\,\mathrm{tgh}\left(\frac{\Omega\hbar}{2K_{\mathrm{B}}T}\right) = \tilde{P}_k(\Omega)\frac{\mathrm{tgh}(\Omega\hbar/2K_{\mathrm{B}}T)}{\Omega\hbar/2K_{\mathrm{B}}T}, \tag{29}$$

where Ω is the variable in the transformed domain and $\tilde{\theta}_k$, $\tilde{Q}_k$, $\tilde{P}_k$ are the transforms of $\tilde{\Theta}_k(t)$, $\tilde{q}_k(t)$, $\tilde{p}_k(t)$, respectively.

Applying the inverse Fourier transform and going back to the Schroedinger picture, we reach the second integral form for Θ_k:

$$\Theta_k = \frac{1}{2\pi}\iint_{\mathcal{R}^2} e^{+i(H_0/\hbar)\xi} p_k\, e^{-i(H_0/\hbar)\xi}\, e^{-i\Omega\xi}\frac{\mathrm{tgh}(\Omega\hbar/2K_{\mathrm{B}}T)}{\Omega\hbar/2K_{\mathrm{B}}T}\,\mathrm{d}\xi\,\mathrm{d}\Omega. \tag{30}$$

In eqs. (29) and (30) it is quite easy to foresee the closeness between Θ_k and p_k, but this becomes far clearer when we express Θ_k in the energy eigenstate basis:

$$(\Theta_k)_{nm} = \frac{2mK_{\mathrm{B}}T}{\hbar} i(p_k)_{nm}\,\mathrm{tgh}\left(\frac{E_n - E_m}{2K_{\mathrm{B}}T}\right) = (p_k)_{nm}\frac{\mathrm{tgh}((E_n - E_m)/2K_{\mathrm{B}}T)}{(E_n - E_m)/2K_{\mathrm{B}}T}, \tag{31}$$

where $\{E_n\}$ is the set of the eigenvalues of H_0.

If we consider the energy representation of a system without eigenvalue degeneracy, both formulas (22) and (30) lead, after some calculations, to the expression (31). In other cases, *e.g.*, when some eigenvalues are degenerate or when we have to deal with any different basis, expression (22) is more useful than eq. (30) to obtain a set of closed form expressions for the friction operator entries. Conversely, as we will explain in the next section, formulas (29) and (30) are very useful in giving a physical interpretation of the friction operators.

For example, if we consider the one-dimensional harmonic oscillator with Hamiltonian $H = p^2/(2m) + (1/2)m\omega^2 q^2$ and we use the energy representation related to the eigenvalues $E_n = (n + 1/2)\hbar\omega$, we easily obtain $\Theta = p\,\mathrm{tgh}(\hbar\omega/2K_{\mathrm{B}}T)/(\hbar\omega/2K_{\mathrm{B}}T)$. In this very simple case the operator Θ is directly proportional to p by means of a constant factor $\mathrm{tgh}(\hbar\omega/2K_{\mathrm{B}}T)/(\hbar\omega/2K_{\mathrm{B}}T)$.

5. – Physical interpretation of friction operator

In a closed system the mean value of any observable can be expressed as follows:

$$\langle O(t)\rangle = \mathrm{Tr}(O\rho) = \sum_{mn} O_{mn}\rho_{nm}(t)\,, \tag{32}$$

in any given basis.

In energy representation it becomes

$$\langle O(t)\rangle = \sum_{mn} O_{mn}\exp\left[\frac{E_n - E_m}{i\hbar}t\right]\rho_{nm}(0). \tag{33}$$

That is to say that the mean value is the sum of a constant term ($n = m$) and some other oscillating terms at the frequency

$$\upsilon = \left| \frac{E_n - E_m}{h} \right|. \tag{34}$$

All these terms are multiplied by a factor proportional to O_{mn}.

Now we define a macroscopic observable as the one lacking of any high-frequency term, whichever the initial conditions $\rho(0)$ are [23].

Thus, we assert that, in energy representation, for the operator O corresponding to such an observable, there holds

$$O_{mn} \cong 0 \quad \text{if } |n - m| > M, \tag{35}$$

where M is any given positive integer.

In other words, the observable corresponding to O is slowly varying, lacking of any rapid fluctuations, and thus nearly diagonal in energy representation.

Accordingly, if we damp the very off-diagonal entries in the energy representation of a generic operator, we "kill" the high-frequency contributions to its time evolution and, therefore, we take its macroscopic counterpart. We shall show later that similar properties hold also in the case of a system in thermal contact with a bath. To sum up, if we look at eq. (29) or (31) we easily understand that the operators Θ_k are the corresponding of p_k "filtered" in such a way that high frequencies are damped by a factor $\mathrm{tgh}(h\upsilon/2K_{\mathrm{B}}T)/(h\upsilon/2K_{\mathrm{B}}T)$, and thus Θ_k are the macroscopic counterpart of p_k. We would like to remark that the lower the temperature, the narrower the filtering is. This is reasonable because mesoscopic and macroscopic kinetic phenomena have noticeable amount of fluctuations in high-temperature condition.

6. – Comparison with the GME

In this section we will show that eq. (18) is a specific case of the GME [12]. In fact, eq. (18) can be recast into the following form:

$$\frac{\mathrm{d}}{\mathrm{d}t} E\{\rho\} = \frac{1}{i\hbar} \big[H_0, E\{\rho\}\big] + R\big(E\{\rho\}\big), \tag{36}$$

where R is our version of the relaxation superoperator

$$R\big(E\{\rho\}\big) = \frac{\beta}{2i\hbar} \sum_{i=1}^{3N} \big[q_i, \Theta_i E\{\rho\} + E\{\rho\}\Theta_i\big] - \frac{Dm^2}{\hbar^2} \sum_{i=1}^{3N} \big[q_i, \big[q_i, E\{\rho\}\big]\big]. \tag{37}$$

The energy representation of eq. (36) is

$$\left[\frac{\mathrm{d}}{\mathrm{d}t} E\{\rho\}\right]_{nm} = \frac{1}{i\hbar} \big(E_n - E_m\big) E\{\rho_{nm}\} + \sum_{k,j} R_{nmkj} E\{\rho_{kj}\}, \tag{38}$$

where the relaxation matrix is

$$R_{nmkj} = -\delta_{mj} \sum_l \Gamma^+_{nllk} + \Gamma^+_{jmnk} + \Gamma^-_{jmnk} - \delta_{nk} \sum_l \Gamma^-_{jllm} \tag{39}$$

and the complex damping parameters are

$$\Gamma^-_{abcd} = \frac{K_\mathrm{B} T \beta m}{\hbar^2} \sum_{i=1}^{3N} (q_i)_{ab} (q_i)_{cd} \frac{\exp[-(E_b - E_a)/2K_\mathrm{B}T]}{\cosh((E_b - E_a)/2K_\mathrm{B}T)}\,, \tag{40}$$

$$\Gamma^+_{abcd} = \frac{K_\mathrm{B} T \beta m}{\hbar^2} \sum_{i=1}^{3N} (q_i)_{ab} (q_i)_{cd} \frac{\exp[+(E_d - E_c)/2K_\mathrm{B}T]}{\cosh((E_d - E_c)/2K_\mathrm{B}T)}. \tag{41}$$

Moreover, as it can be easily proved, our expression for the relaxation matrix fulfils the following properties:

$$\sum_m R_{mmpn} = 0, \qquad \forall pn, \tag{42}$$

$$R^*_{pmjn} = R_{mpnj}, \qquad \forall pmjn, \tag{43}$$

$$R_{mmmm} < 0, \qquad \forall m, \tag{44}$$

$$R_{mmnn} > 0, \qquad \forall mn, m \neq n. \tag{45}$$

Equations (38) and (39) represent rigorously the form of the GME as it can be found in the literature [12], where the relaxation matrix fulfils the same properties (42)-(45). In addition, eqs. (40) and (41) give a close form of $\Gamma^\pm$ in the case of a system whose energy exchange with a reservoir is modelled by friction and noise.

7. – Secular approximation

As is shown in the literature [12] the GME can be simplified by means of the so-called secular approximation.

This approximation leads eqs. (38) and (39) to the Pauli master equation for the populations:

$$\left(\frac{\mathrm{d}}{\mathrm{d}t} E\{\rho\}\right)_{nn} = \sum_i W_{ni} E\{\rho_{ii}\} - \left(\sum_i W_{in}\right) E\{\rho_m\} \tag{46}$$

and to the following equation for the coherence terms:

$$\left[\frac{\mathrm{d}}{\mathrm{d}t} E\{\rho\}\right]_{nm} = \frac{1}{i\hbar}(E_n - E_m) E\{\rho_m\} - \gamma_{nm} E\{\rho_{nm}\}, \tag{47}$$

where W_{ni} are the transition probabilities

$$W_{nm} = \Gamma^+_{mnnm} + \Gamma^-_{mnnm} \tag{48}$$

and

$$\gamma_{nm} = \sum_k \Gamma^+_{nkkn} - \Gamma^+_{mmnn}\Gamma^-_{mmnn} + \sum_k \Gamma^-_{mkkm}\,. \tag{49}$$

According to our model, their close form relationships with the q_i are

$$W_{nm} = \frac{2K_{\mathrm{B}}T\beta m}{\hbar^2}\sum_{k=1}^{3N}|(q_i)_{mn}|^2\frac{\exp[(E_m-E_n)/2K_{\mathrm{B}}T]}{\cosh((E_m-E_n)/2K_{\mathrm{B}}T)}, \tag{50}$$

$$\begin{aligned}\gamma_{nm} = {} & \frac{K_{\mathrm{B}}T\beta m}{\hbar^2}\times \\ & \times\sum_{k,j}\left[|(q_i)_{nj}|^2\frac{\exp[(E_n-E_j)/2K_{\mathrm{B}}T]}{\cosh((E_n-E_j)/2K_{\mathrm{B}}T)}+|(q_i)_{mj}|^2\frac{\exp[(E_m-E_j)/2K_{\mathrm{B}}T]}{\cosh((E_m-E_j)/2K_{\mathrm{B}}T)}\right]- \\ & -\frac{2K_{\mathrm{B}}T\beta m}{\hbar^2}\sum_k\left[(q_i)_{mm}(q_i)_{nn}\right].\end{aligned} \tag{51}$$

The matrix entries W^{-1}_{nm} and γ^{-1}_{nm} play the role of quantum relaxation times.

As one can see, eq. (50) is a specific case of the Fermi golden rule for open systems, where

$$\frac{W_{nm}}{W_{mn}} = \frac{\exp[-(E_n/K_{\mathrm{B}}T)]}{\exp[-(E_m/K_{\mathrm{B}}T)}\,. \tag{52}$$

Observing eqs. (46) and (47) one can also agree that the comments at the end of sect. **5** are still acceptable in the case of systems coupled with a thermal bath, because the modification of the harmonic spectrum is negligible.

* * *

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Appendix

Multiplicative noise in Langevin-type equations

In this appendix we prove a theorem that allows to derive the expectation value of a state vector, which evolves in time fulfilling a Langevin equation driven by multiplicative Gaussian noise.

Theorem: The evolution equation for the expectation value of ρ in eq. (15) with Gaussian noise subjected to eqs. (2) and (3) is

$$\frac{\mathrm{d}}{\mathrm{d}t}E\{\mathbf{x}\} = AE\{\mathbf{x}\} + \sum_i B_i^2\{\mathbf{x}\}. \tag{A.1}$$

Proof: By using eq. (15) and the properties of the noise, the corresponding Fokker-Planck equation [19] is

$$\frac{\mathrm{d}}{\mathrm{d}t}W(\mathbf{x},t) = -\sum_i \frac{\partial}{\partial x_i}\left\{\left[\sum_j a_{ij}x_j + \sum_{k,j,p} b_{kpj}x_p b_{ikj}\right]W\right\} + \\ + \sum_{i,j}\frac{\partial^2}{\partial x_i\,\partial x_j}\left\{\left[\sum_{k,n,m} b_{ink}x_n b_{jmk}x_m\right]W\right\}, \tag{A.2}$$

where $[A]_{ij} = a_{ij}$ and $[B_j]_{nm} = b_{nmj}$.

The expectation value of a column vector component is given by

$$E\{x_b(t)\} = \int_{\mathcal{R}^n} x_b W\,\mathrm{d}\mathbf{x}. \tag{A.3}$$

By differentiating with respect to the time, using eqs. (A.3) and (A.2) and recalling the well-known property

$$\int_{\mathcal{R}^n}\Theta(\mathbf{x})\frac{\partial\lambda(\mathbf{x})}{\partial x_k}\,\mathrm{d}\mathbf{x} = -\int_{\mathcal{R}^n}\lambda\mathbf{x}\frac{\partial\Theta(\mathbf{x})}{\partial x_k}\mathrm{d}\mathbf{x}, \tag{A.4}$$

one obtains, after some straightforward calculations, the final relationships

$$\int_{\mathcal{R}^4} x_b\frac{\mathrm{d}W}{\mathrm{d}t}\mathrm{d}\mathbf{x} = \sum_j a_{bj}\int_{\mathcal{R}^4} x_j W\,\mathrm{d}\mathbf{x} + \sum_{k,j,p} b_{kpj}b_{bkj}\int_{\mathcal{R}^4} x_p W\,\mathrm{d}\mathbf{x}, \quad \forall b. \tag{A.5}$$

This is the explicit form of the projection of eq. (A.1) on a given basis.

REFERENCES

[1] Abragam A., *The Principles of Nuclear Magnetism* (Oxford, Clarendon Press) 1961.
[2] Slichter C. P., *Principles of Magnetic Resonance* (Springer Verlag) 1990.
[3] Shore W., *The Theory of Coherent Atomic Excitation* (John Wiley & Sons) 1990.
[4] Sargent M., Scully M. O. and Lamb W. E., *Laser Physics* (Addison-Wesley) 1974.
[5] Feldman B. J. and Feld M. S., *Phys. Rev. A*, **5** (1972) 899.
[6] Teich W. G. and Mahler G., *Phys. Rev. A*, **45** (1992) 3300.
[7] Palma G. M., Suominen K. and Ekert A. K., *Proc. R. Soc. London Ser. A*, **452** (1996) 567.
[8] Chuang I. L., Laflamme R., Shor P. W. and Zurek W. H., *Science*, **270** (1995) 1635.
[9] Chiabrera A., Bianco B. and Moggia E., *Bioelectrochem. Bioenerg.*, **28** (1992) 355.
[10] Moggia E., Chiabrera A. and Bianco B., *J. Appl. Phys.*, **82** (1997) 4669.
[11] Landau L. and Lifshitz E. M., *Quantum Mechanics: Non Relativistic Theory* (MIR, Moscow) 1991.
[12] Blum K., *Density Matrix Theory and Applications* (Plenum Press, New York) 1981.
[13] Mahler G. and Weberruss V. A., *Quantum Networks: Dynamics of Open Nanostructures* (Springer Verlag, Berlin) 1995.
[14] Caldirola P. and Lugiato L. A., *Physica A*, **116** (1982) 248.
[15] Caldirola P., *Nuovo Cimento B*, **77** (1983) 241.

[16] Caldeira A. O. and Leggett A. J., *Physica A*, **121** (1983) 587.
[17] Kleinert H. and Shabanov S. V., *Phys. Lett. A*, **200** (1995) 224.
[18] Tsusaka K., *Phys. Rev. E*, **59** (1999) 4931.
[19] Risken H., *The Fokker-Planck Equation* (Springer, Berlin) 1989.
[20] Messiah A., *Mecanique Quantique* (Dunod, Paris) 1962.
[21] Schiff L. I., *Quantum Mechanics* (Mc Graw Hill, New York) 1968.
[22] Bellmann R., *Introducion to Matrix Analysis* (Mc Graw Hill, New York) 1960.
[23] van Kampen N. G., *Physica A*, **153** (1988) 97.