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Dissipative quantum dynamics, entropy production and irreversible evolution towards equilibrium

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Abstract. A non-linear evolution equation for the density operator is proposed which models the irreversible dissipative time evolution of a system in contact with its surroundings. Various properties of the proposed equation are discussed. As an illustration the three-state system is studied in detail.

1. Introduction

The problem of dissipative quantum evolution and irreversibility has attracted a lot of interest, especially during the past two decades. Reviews containing numerous references have been written by various authors; we would like to mention especially those by Hasse (1975), Messer (1979) and Dekker (1981). Dekker's article is restricted to the damped harmonic oscillator, a system whose quantum dynamics has attracted much attention because of its 'simplicity'. Even this simplified problem is far from being solved. Much less understood is, of course, the general problem of dissipation in quantum mechanics.

In the following we construct a phenomenological equation of motion which describes dissipative dynamics. It may be helpful to visualise, as a typical situation, the time evolution of a 'small' subsystem of a big one, where the 'big' system as well as the coupling to the small one are not known in detail. We are only interested in the dynamics of the subsystem and we want to model its time development in a more or less phenomenological way. The resulting equation will be the non-linear differential equation for the density operator.

Non-linear quantum evolution equations have been proposed previously by a number of authors. Kostin (1972, 1975) proposed a non-linear Schrödinger equation

$$\dot{\psi} = \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \Delta + V \right) \psi - \frac{\gamma}{2} \left(\ln \frac{\psi}{\psi^*} - \left\langle \ln \frac{\psi}{\psi^*} \right\rangle \right) \psi \quad (1.1)$$

which has certain drawbacks and therefore Schuch *et al* (1983, 1984a, b) recently proposed and motivated a modified equation

$$\dot{\psi} = \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \Delta + V \right) \psi - \gamma (\ln \psi - \langle \ln \psi \rangle) \psi. \quad (1.2)$$

In both equations the Schrödinger equation is modified by adding a phenomenological dissipative—or frictional—term which includes a logarithmic non-linearity. γ is a phenomenological constant. The subtracted average value $\langle \ln \psi \rangle$ is responsible for conservation of the normalisation. A different, related, equation has been given by

Gisin (1981a, b, 1982a, b, 1983a, b, 1986). Gisin studied the equation

$$|\dot{\psi}\rangle = \frac{1}{i\hbar} H|\psi\rangle - \gamma(A - \langle A \rangle)|\psi\rangle \quad (1.3)$$

where H is the Hamiltonian and A is a Hermitian operator. Again the term $\langle A \rangle|\psi\rangle$ guarantees conservation of norm. The nature of the operator A depends on the system under consideration, in particular the case $A = H$ has been studied by Gisin. Different non-linear Schrödinger equations have been proposed by various authors (for a discussion see Hasse (1975) or Schuch *et al* (1983)).

Two remarks should be made: first, (1.1) and (1.2) are given only in the position representation. A generalisation to a representation-free equation (like (1.3)) has not been given. Second, it should be stressed that the non-linear Schrödinger equations are intrinsically equations for the wavefunction or the state vector, i.e. they describe the time evolution of pure states. A pure state can, however, be considered as a highly exceptional state which must be carefully prepared. Any perturbation by contact with the surroundings is likely to destroy the pure state nature of the system. Note also—from the viewpoint of subsystem dynamics—that the state of a subsystem is generally *not* pure, even if the whole system is. If the subsystem is initially in a pure state, this property is generally destroyed when time increases. (Here the state of the subsystem is as usual defined by taking the partial trace of the density operator over the other degrees of freedom.)

Most of the evolution equations for the statistical operator proposed until now, which should describe dissipative effects or subsystem dynamics, are linear. They are known as generalised—or Markovian—master equations. For a rigorous mathematical treatment see the monograph by Davies (1976) or the paper by Gorini *et al* (1978), where one can also find the concept of quantum dynamical semigroups which was investigated by several authors (for example, Lindblad 1976, 1983). Non-linear evolution equations for the statistical operator are rarely found in the literature. Messer and Baumgartner (1978) defined a non-linear ‘dissipative von Neumann equation corresponding to a dissipative Schrödinger equation’, and Beretta *et al* (1984, 1985) proposed a non-linear evolution for the statistical operator, which will be discussed later.

It is the opinion of these authors that the phenomenological dissipative relaxation of a system should be preferably described by a non-linear equation of motion for the density operator. It is the purpose of this paper to present such a new equation. Section 2 discusses the case of a free dissipative relaxation. In § 3 we consider the coupling to an energy (heat) bath as well as the constrained time evolution where the expectation value of the energy is kept constant in time. Section 4 generalises the equations. Section 5 contains some concluding remarks. In the present paper we restrict ourselves to the presentation of the basic theory, illustrated by some simple examples. A forthcoming article will discuss applications to more complicated (and physically more relevant) systems.

2. Dissipative evolution

The time evolution of the density matrix ρ for the system under consideration—specified by the Hamiltonian H —can be written as

$$\dot{\rho} = \frac{1}{i\hbar} [H, \rho] + \gamma D(\rho) \quad (2.1)$$

where $D(\rho)$ is a dissipative operator, which is still to be determined. Equation (2.1) implies, of course, that memory effects are neglected, i.e. $\dot{\rho}(t)$ depends only on the momentary $\rho(t)$ and not on its history $\rho(t')$, $t' < t$. The real constant γ measures the strength of the dissipative term. For $\gamma = 0$ we have ordinary quantum evolution according to the von Neumann equation

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] \tag{2.2}$$

which conserves the von Neumann entropy $\langle S \rangle = \text{Tr } \rho S$ where we have used the notation

$$S = -\ln \rho. \tag{2.3}$$

It is worthwhile recalling that (2.2) conserves $\langle S \rangle$ for pure states ($\rho^2 = \rho$) as well as for mixed states ($\rho^2 \neq \rho$). In the following any time evolution of ρ is called 'dissipative' if it does not conserve the entropy $\langle S \rangle$.

In order to 'derive' an explicit expression for the dissipative operator $D(\rho)$ we adopt the strategy to look for the most intuitive and simple form satisfying a few necessary conditions.

(i) $\text{Tr } \rho = 1$ is conserved.

(ii) $\rho(t)$ must remain Hermitian or—more specifically—positive.

(iii) The time evolution of two independent systems which are not related by any coupling, constraints, etc, must be independent, i.e. for $H = H_1 + H_2$ we require $\rho(t) = \rho_1(t) \otimes \rho_2(t)$.

Eventually the resulting expression for $D(\rho)$ will be unique (it will not) or the uniqueness of $D(\rho)$ may be achieved by extending conditions (i)–(iii) by additional reasonable properties of $D(\rho)$. Restated for $D(\rho)$, the conditions (i)–(iii) are

$$(i)' \quad \text{Tr } D(\rho) = 0 \tag{2.4a}$$

$$(ii)' \quad D(\rho)^+ = D(\rho) \tag{2.4b}$$

$$(iii)' \quad D(\rho_1 \otimes \rho_2) = D(\rho_1) \otimes \rho_2 + \rho_1 \otimes D(\rho_2). \tag{2.4c}$$

Equation (2.4c) can be easily derived by demanding that $\rho_1 \otimes \rho_2$ satisfies (2.1) for $H = H_1 + H_2$ and ρ_1, ρ_2 both satisfy (2.1) for H_1, H_2 , respectively. Introducing the operator \tilde{D} by

$$D(\rho) = \tilde{D}(\rho)\rho \tag{2.5}$$

equation (2.4c) can be written as

$$\tilde{D}(\rho_1 \otimes \rho_2)(\rho_1 \otimes \rho_2) = \tilde{D}(\rho_1)\rho_1 \otimes \rho_2 + \rho_1 \otimes \tilde{D}(\rho_2)\rho_2 \tag{2.6}$$

which implies

$$\langle \tilde{D}(\rho_1 \otimes \rho_2) \rangle = \langle \tilde{D}(\rho_1) \rangle + \langle \tilde{D}(\rho_2) \rangle \tag{2.7}$$

i.e. additivity of the functional $\langle \tilde{D}(\rho) \rangle$.

A solution of the functional equation (2.6) is given by

$$\tilde{D}_1(\rho) = -\ln \rho = S \tag{2.8}$$

as well as by

$$\tilde{D}_2(\rho) = \langle -\ln \rho \rangle \rho \tag{2.9}$$

or by any linear combination of \tilde{D}_1 and \tilde{D}_2 . We can satisfy the probability conservation (2.4a) by

$$\tilde{D}(\rho) = S - \langle S \rangle \mathbb{1} \tag{2.10}$$

or

$$D(\rho) = (S - \langle S \rangle \mathbb{1})\rho. \tag{2.11}$$

$D(\rho)$ is obviously Hermitian. This is, however, not the only possible functional form satisfying (2.4a)-(2.4c). In particular

$$D_A(\rho) = \frac{1}{2}[A, \rho]_+ - \langle A \rangle \rho \tag{2.12}$$

where A is a Hermitian operator and $[,]_+$ denotes the anticommutator, is traceless, Hermitian and—with $A = A_1 + A_2$ —satisfies the functional equation (2.4c).

It has been shown (see, e.g., Ochs (1975) or the review article on entropy by Wehrl (1978) and references therein) that if we demand subadditivity,

$$\langle S(\rho) \rangle \leq \langle S(\rho_1) \rangle + \langle S(\rho_2) \rangle = \langle S(\rho_1 \otimes \rho_2) \rangle \tag{2.13}$$

where the systems 1 and 2 are no longer supposed to be independent, then the only possible functional forms are $S = -\ln \rho$ or the Hartley entropy (=logarithm of the number of eigenvalues of ρ different from zero). It should also be noted that there is another possibility of deriving the entropy functional from a set of three axioms (see, e.g., the concise presentation by Thirring (1980)).

In the following we adopt the choice (2.11), i.e. we consider the generalised von Neumann equation

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] + \gamma(S - \langle S \rangle \mathbb{1})\rho. \tag{2.14}$$

Equation (2.14) describes the free dissipative time evolution, i.e. no additional conditions or constraints are imposed. In the remainder of this section we study the properties of (2.14) assuming, for simplicity, a finite-dimensional Hilbert space with dimension n .

It is clear from (2.14) that the equipartition distribution

$$\rho_n = (1/n)\mathbb{1} \tag{2.15}$$

is a stationary solution of (2.14), which has the maximum possible value of the entropy $\langle S(\rho_n) \rangle = \ln n$.

It is useful to convert equation (2.14) for ρ into an equation for the operator $S = -\ln \rho$. Starting from

$$\rho = e^{-S} \tag{2.16}$$

we obtain by differentiation (Wilcox 1967, equations (2.1) and (2.5))

$$\begin{aligned} \dot{\rho} &= - \int_0^1 \exp[-(1-u)S] \dot{S} \exp(-uS) du \\ &= \frac{1}{i\hbar}[H, \exp(-S)] + \gamma(S - \langle S \rangle \mathbb{1}) \exp(-S) \\ &= -\frac{1}{i\hbar} \int_0^1 \exp[-(1-u)S][H, S] \exp(-uS) du \\ &\quad + \gamma \int_0^1 \exp[-(1-u)S](S - \langle S \rangle \mathbb{1}) \exp(-uS) du \end{aligned} \tag{2.17}$$

or

$$\int_0^1 \exp(uS) \left(\dot{S} - \frac{1}{i\hbar}[H, S] + \gamma(S - \langle S \rangle \mathbb{1}) \right) \exp(-uS) du = 0 \tag{2.18}$$

which implies (because e^{uS} is positive for real u) that the term in large brackets vanishes, i.e. S satisfies

$$\dot{S} = \frac{1}{i\hbar}[H, S] - \gamma(S - \langle S \rangle \mathbb{1}). \tag{2.19}$$

Equation (2.19) again shows the stationarity of (2.15).

A direct consequence of (2.19) is the non-decreasing property of the entropy

$$\frac{d}{dt}\langle s \rangle = \text{Tr}(\dot{S}\rho + S\dot{\rho}) = \gamma(\langle S^2 \rangle - \langle S \rangle^2) \geq 0. \tag{2.20}$$

Equation (2.20) determines the sign of the constant γ to be positive. Another consequence of (2.20) are the uniqueness properties of the stationary solution (2.15), because stationarity gives $\langle S^2 \rangle = \langle S \rangle^2$, which implies $\rho = \rho_m = (1/m)\mathbb{1}_m$, where $\mathbb{1}_m$ is the unit operator on a m -dimensional subspace and zero elsewhere. This m -dimensional subspace is spanned by eigenvectors of the Hamiltonian H . The entropy of these stationary solutions is $\langle S \rangle = \ln m$. In particular the pure states ($m = 1$) $\rho = |\psi\rangle\langle\psi|$ and the equipartition distribution $\rho_0 = (1/n)\mathbb{1}$ with entropy $\langle S \rangle = 0$ and $\langle S \rangle = \ln n$ are non-dissipative. Stationary pure states satisfy $[H, \rho] = [H, |\psi\rangle\langle\psi|] = 0$, i.e. $|\psi\rangle$ is an eigenvector of H . The stationary states with $m \neq n$ are, however, unstable. Any small distortion drives the state to the stable maximum entropy solution $\rho_n = (1/n)\mathbb{1}$.

The time dependence of expectation values of an observable B , which may depend explicitly on time, is given by

$$\begin{aligned} \frac{d}{dt}\langle B \rangle &= \text{Tr}\left(\frac{1}{i\hbar}B[H, \rho] + \gamma B(S - \langle S \rangle \mathbb{1})\rho\right) + \left\langle \frac{\partial B}{\partial t} \right\rangle \\ &= \frac{1}{i\hbar}\langle [B, H] \rangle + \gamma(\langle BS \rangle - \langle B \rangle \langle S \rangle) + \left\langle \frac{\partial B}{\partial t} \right\rangle \end{aligned} \tag{2.21}$$

which simplifies if B commutes with H . In particular, we obtain for the expectation value of the energy

$$\frac{d}{dt}\langle H \rangle = \gamma(\langle HS \rangle - \langle H \rangle \langle S \rangle). \tag{2.22}$$

For pure states ($\rho^2 = \rho$) S is equal to zero, i.e. (2.14) reduces to the ordinary von Neumann equation. This shows that (2.14) cannot be identified with the non-linear Schrödinger equation (1.2) for pure states despite structural similarities.

It will be instructive to study the time evolution of the n -state system with time-independent Hamiltonian explicitly. Let us assume that ρ is diagonalised with eigenvalues p_i and normalised eigenvectors $|i\rangle$, which are, of course, time dependent:

$$\rho(t)|i(t)\rangle = p_i(t)|i(t)\rangle. \tag{2.23}$$

ρ is positive with unit trace, which implies $p_i \geq 0$ and $\sum_i p_i = 1$. Taking the time derivatives of (2.23) we obtain

$$(\dot{\rho} - \dot{p}_i \mathbb{1})|i\rangle = (p_i \mathbb{1} - \rho) \frac{d}{dt}|i\rangle \tag{2.24}$$

and, after inserting the generalised von Neumann equation (2.14) and taking matrix elements with $|j\rangle$,

$$\frac{1}{i\hbar} H_{ji}(p_j - p_i) + \delta_{ji}\{-\gamma(\ln p_i + \langle S \rangle)p_i - \dot{p}_i\} = (p_i - p_j)\langle j|\frac{d}{dt}|i\rangle \quad (2.25)$$

$$\langle S \rangle = -\sum_i p_i \ln p_i$$

$$H_{ji} = \langle j|H|i\rangle.$$

The time evolution of the non-diagonal contributions $j \neq i$ is given by

$$\frac{1}{i\hbar} H_{ji}(p_j - p_i) = (p_i - p_j)\langle j|\frac{d}{dt}|i\rangle \quad (2.26)$$

which leads to

$$\langle j|\frac{d}{dt}|i\rangle = \frac{i}{\hbar} H_{ji} \quad (2.27)$$

for $p_i \neq p_j$. Equation (2.27) can be solved for $|i\rangle$ by conventional basis expansion with a time-independent orthonormal basis $|\mu\rangle$

$$|i(t)\rangle = \sum_{\mu} \varphi_{i\mu}(t)|\mu\rangle \quad (2.28)$$

$$\dot{\varphi}_{i\nu} = \frac{i}{\hbar} \sum_{\mu} \tilde{H}_{\nu\mu} \varphi_{i\mu} \quad (2.29)$$

where the $\tilde{H}_{\nu\mu}$ are matrix elements with respect to the basis $|\mu\rangle$: $\tilde{H}_{\nu\mu} = \langle \nu|H|\mu\rangle$. It should be noted that this evolution is non-dissipative, i.e. independent of γ . The eigenstates of ρ evolve exactly as those satisfying the usual von Neumann equation. More interesting is the time evolution of the eigenvalues: the diagonal part of (2.25) gives

$$\dot{p}_i = -\gamma(\ln p_i + \langle S \rangle)p_i. \quad (2.30)$$

First we observe again that $\langle S \rangle$ is non-decreasing, as already shown above:

$$\begin{aligned} \frac{d}{dt}\langle S \rangle &= -\sum_i \dot{p}_i \ln p_i \\ &= \gamma \sum_i (\langle S \rangle + \ln p_i)p_i \ln p_i \\ &= \gamma(\langle S^2 \rangle - \langle S \rangle^2) \geq 0. \end{aligned} \quad (2.31)$$

As a further consequence one can show that the time evolution (2.30) is mixing enhancing (compare Wehrl 1978, § II.C), which is a stronger property than entropy increasing. Details are given in the appendix.

Equation (2.30) also conserves positivity of ρ , since no eigenvalue of ρ can cross zero ($p_j(t_0) = 0$ implies $p_j(t) = 0$ for $t > t_0$). Stationary eigenvalues $\dot{p}_i = 0$ are found for

$$\begin{aligned} \text{(i)} \quad & p_i = 0 \\ \text{(ii)} \quad & -\ln p_i = \langle S \rangle \quad \text{for } p_i \neq 0. \end{aligned} \quad (2.32)$$

A density with no initial population of state i will never populate this state. (ii) implies that for $p_i \neq 0$ all stationary p_i are equal and hence we have

$$p_i = 1/m \quad \text{for } p_i(t_0) \neq 0 \quad (2.33)$$

where m counts the p_i different from zero. The only stable stationary distribution is the maximum entropy equipartition distribution $\rho_n = (1/n)\mathbb{1}$, where 'stable' means that any small perturbation of ρ_n will evolve back towards it. In other words, ρ_n is the only stable attractor and the basin of attraction (the set of all ρ , which develop asymptotically towards ρ_n) consists of all ρ with $p_i \neq 0, i = 1, \dots, n$.

Let us look at the simple case of two- and three-state dynamics in more detail. In the two-state case we have two eigenvalues of ρ : p and $q = 1 - p$. Equation (2.30) reduces to a single differential equation for p :

$$\begin{aligned} \dot{p} &= -\gamma(\ln p + \langle S \rangle)p \\ &= \gamma p(1-p) \ln[(1-p)/p] \end{aligned} \tag{2.34}$$

where

$$\langle S \rangle = -p \ln p - (1-p) \ln(1-p) \tag{2.35}$$

has been inserted. For $p = \frac{1}{2}$ we have $\dot{p} = 0$ and for $p = \frac{1}{2} + u$ linearisation of (2.34) yields $\dot{u} = -\gamma u$ and hence $u = u_0 \exp[-\gamma(t - t_0)]$ or

$$p = \frac{1}{2} + (p_0 - \frac{1}{2}) \exp[-\gamma(t - t_0)] \tag{2.36}$$

i.e. we have an exponential decay towards equilibrium.

Entropy $\langle S \rangle$ and \dot{p} are shown in figure 1. The stable (maximum entropy) and unstable stationary distributions are marked by circles. After separation of variables and substitution of $x = (1-p)/p$, (2.34) can be integrated in closed form:

$$p(t) = \left[1 + \left(\frac{1}{p_0} - 1 \right) \exp[-\gamma(t - t_0)] \right]^{-1} \tag{2.37}$$

with $p_0 = p_0(t_0)$. For $t \rightarrow \infty$, $p(t)$ converges to the equilibrium value of $\frac{1}{2}$, provided, of course, that $p_0 \neq 0$. The time dependence $p(t)$ is shown in figure 2.

The three-state case is less trivial. The state with eigenvalues p_1, p_2, p_3 can be conveniently described in a triangular plot, where each state $\{(p_1, p_2, p_3) | p_1, p_2, p_3 \geq 0, p_1 + p_2 + p_3 = 1\}$ is represented as a point in the interior of an equilateral triangle with unit height. The entropy $\langle S \rangle$ is shown in figure 3(a) and the time evolution is depicted in figure 3(b), which shows the time dependence of the eigenvalues p_i . The boundary equilibria are unstable stationary points and all states approach the maximum entropy equipartition distribution $p_1 = p_2 = p_3 = \frac{1}{3}$, except those on the boundary.

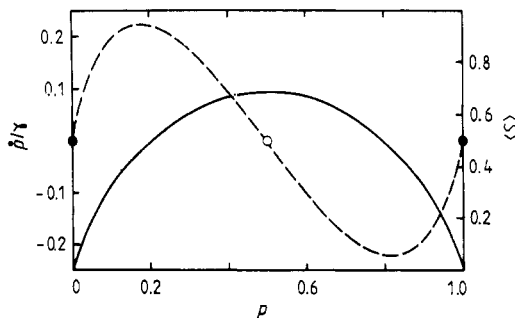


Figure 1. Two-state system. Entropy $\langle S \rangle$ (—) and time derivative of the probability p to be in state 1 (---). The stable (○) and unstable (●) stationary distributions are marked.

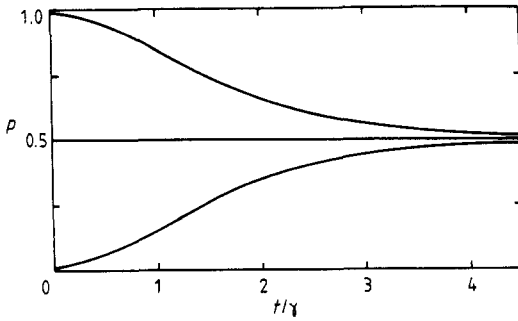


Figure 2. Two-state system. Time dependence of the probability $p(t)$ given in (2.33) for three initial values of p (0.01, 0.5, 0.99). The state $p = 0.5$ is the stable equilibrium distribution.

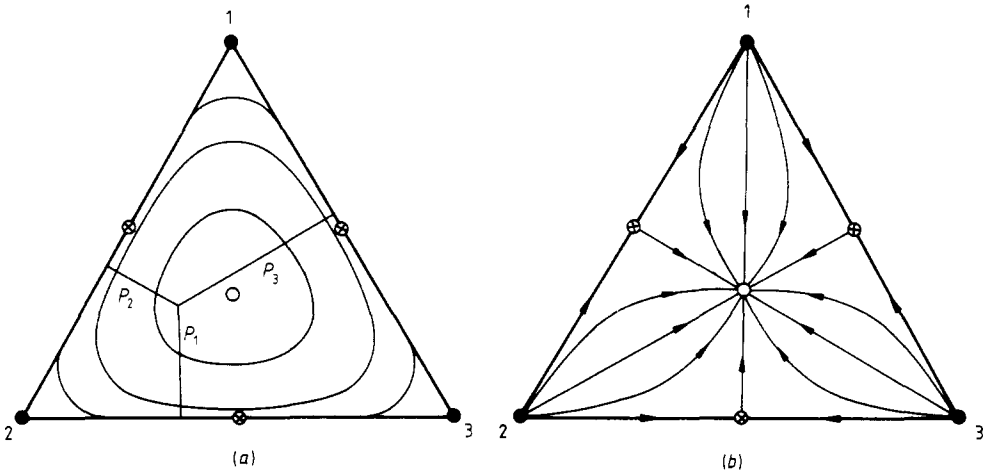


Figure 3. Three-state system. The distances from the sides of the state triangle are the probabilities p_1, p_2, p_3 , summing to unity. (a) shows contours of constant entropy $\langle S \rangle$. The maximum of the entropy (○) is marked as well as the three saddle points (⊗) and the pure states at the corners with zero entropy (●). (b) shows the time variation of the p_i , i.e. a phase portrait of the probability flow. There is a stable attractor at the centre (○) and three unstable saddle points (⊗).

3. Coupling to baths and constrained systems

In the preceding section we discussed the free dissipative evolution of the density operator, i.e. systems with no constraints whatsoever. In this case the density matrix evolves with increasing entropy towards the equipartition distribution. Such a time evolution models phenomenologically a system coupled in an undefined way to an undefined surrounding. ‘Undefined’ means that nothing is known about the nature of, and the coupling to, the surroundings. In this case any ignorance in the initial state (i.e. non-purity) will magnify and develop towards states with maximum uncertainty. Completely prepared states (pure states) evolve with no dissipation, i.e. they remain pure, which is, of course, an idealised situation. If we have some knowledge about the coupling of the system to the surroundings we are forced to incorporate this knowledge into the equations of motion.

3.1. Coupling to a bath

The most prominent case is the coupling to a ‘bath’, which means a ‘big’ system, characterised by a constant mean value of an observable A and the fact that the ‘bath’ is not influenced by our ‘small’ system. Let us—for simplicity—assume a coupling to a heat bath ($A = H$). The general case will be discussed in § 4. Intuitively the states with an energy exceeding the system’s average energy will tend to be depopulated, the others will tend to increase, which can be phenomenologically modelled by an additional term proportional to $(H - \langle H \rangle \mathbb{1})\rho$ in the dissipative von Neumann equation. This term is non-Hermitian, however, which results in a non-Hermitian time development of $\rho(t)$. Choosing the usual recipe to symmetrise by replacing $H\rho$ by the Hermitian operator $\frac{1}{2}[H, \rho]_+$ ($[,]_+$ is the anticommutator) we finally obtain

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] + \gamma\{(S - \langle S \rangle \mathbb{1})\rho - \beta(\frac{1}{2}[H, \rho]_+ - \langle H \rangle \rho)\} \tag{3.1}$$

with a real coupling constant β .

Let us first show that the canonical distribution

$$\rho_c = \frac{1}{Z} \exp(-\beta H) = \exp(-\chi - \beta H) \tag{3.2}$$

with the partition function

$$Z = Z(\beta) = \text{Tr } e^{-\beta H} = e^\chi \tag{3.3}$$

is a stationary solution of (3.1).

First we note that $[H, \rho_c] = 0$ and second we have

$$\begin{aligned} S_c &= -\ln \rho_c = \chi \mathbb{1} + \beta H \\ \langle S_c \rangle &= \chi + \beta \langle H \rangle \\ \frac{1}{2}[H, \rho_c]_+ &= H\rho_c \end{aligned} \tag{3.4}$$

and hence

$$\begin{aligned} (S_c - \langle S_c \rangle \mathbb{1})\rho_c - \beta(\frac{1}{2}[H, \rho_c]_+ - \langle H \rangle \rho_c) \\ = [\chi \mathbb{1} + \beta H - (\chi + \beta \langle H \rangle) \mathbb{1}]\rho_c - \beta(H\rho_c - \langle H \rangle \rho_c) = 0. \end{aligned} \tag{3.5}$$

We therefore identify the constant β with the reciprocal average energy (temperature) of the heat bath:

$$\beta = 1/kT. \tag{3.6}$$

The expectation value of an observable B satisfies

$$\frac{d}{dt}\langle B \rangle = \frac{1}{i\hbar}\langle [B, H] \rangle + \gamma[\langle BS \rangle - \langle B \rangle \langle S \rangle - \beta(\frac{1}{2}\langle [B, H]_+ \rangle - \langle B \rangle \langle H \rangle)] + \left\langle \frac{\partial B}{\partial t} \right\rangle \tag{3.7}$$

in particular the time derivative of the energy is given by

$$\frac{d}{dt}\langle H \rangle = -\gamma[\langle HS \rangle - \langle H \rangle \langle S \rangle - \beta(\langle H^2 \rangle - \langle H \rangle^2)]. \tag{3.8}$$

The entropy $\langle S \rangle$ is generally *not* increasing for $\beta \neq 0$. Starting with an initial equipartition distribution, which has maximum possible entropy, the system will evolve towards the canonical distribution (3.2), which has lower entropy $\langle S_c \rangle$.

Again we study the time evolution of a n -state system in more detail. In the same way as for the free dissipation in § 2 we obtain the first-order system of non-linear differential equations

$$\dot{p}_i = -\gamma[\ln p_i + \langle S \rangle + \beta(H_{ii} - \langle H \rangle)]p_i \tag{3.9}$$

with $H_{ii} = \langle i|H|i \rangle$, which generalises (2.30). Again positivity of ρ is guaranteed.

In a similar way to § 2 we find stationary distributions $\dot{p}_i = 0, i = 1, \dots, n$. If all p_i are different from zero the system evolves towards the canonical distribution (3.2)

$$p_i = \exp(-\chi - \beta \epsilon_i) \tag{3.10}$$

where the ϵ_i are eigenvalues of the Hamiltonian. It can be easily shown that the eigenstates $|i \rangle$ of ρ approach those of H for $t \rightarrow \infty$, i.e. $H_{ii} \rightarrow \epsilon_i$. If one or more of the p_i are initially zero, this property is conserved ($\dot{p}_i \sim p_i$) and the system evolves toward the unstable equilibria (saddle points) at the boundary of state space.

Let us look at a three-state case in more detail. For simplicity we assume equidistant energy eigenvalues $\epsilon_1 = 0, \epsilon_2 = \epsilon, \epsilon_3 = 2\epsilon$ and measure energy in units of ϵ . The average energy is $\langle H \rangle = p_2 + 2p_3$. Lines of constant energy $\langle H \rangle$ in the state space triangle are straight lines in this case, which are orthogonal to the boundary $p_2 = 0$ (compare figure 6 below). Figure 4 shows the time development of the p_i for $\beta = \ln 2$ (i.e. $e^{-\beta} = \frac{1}{2}$). The stable canonical equilibrium distribution is $(p_1, p_2, p_3) = (\frac{4}{7}, \frac{2}{7}, \frac{1}{7})$ with $\langle H \rangle = \frac{4}{7}$. Unstable equilibria (canonical two-state distributions) on the boundary (\otimes) are found at $(\frac{2}{3}, \frac{1}{3}, 0), (\frac{4}{5}, 0, \frac{1}{5})$ and $(0, \frac{2}{3}, \frac{1}{3})$. Structurally the flow lines are similar to the free case shown in figure 3(b), however distorted.

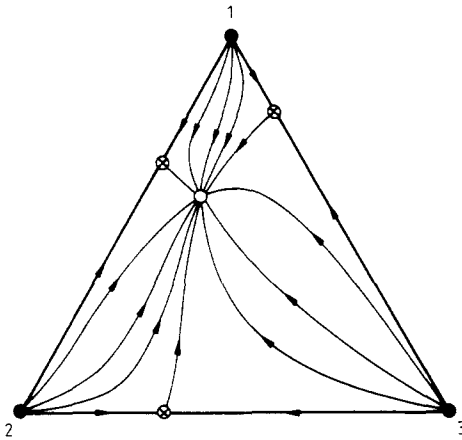


Figure 4. Phase portrait of a three-state system in contact with a heat bath (equation (3.1)) for $\beta = \ln 2$. The energies of the states 1, 2, 3 are 0, 1, 2, respectively. The canonical (Boltzmann) distribution (O) is a stable attractor. Unstable equilibria (\otimes) are situated on the boundaries (two-state Boltzmann distributions).

Let us now discuss some limit cases. For an infinitely hot reservoir ($\beta = 0$) equation (3.1) reduces to the free (unconstrained) case discussed in § 2.

In the case $\beta \gg 1$ (low temperature of the heat bath) the term $\gamma(S - \langle S \rangle)$ can be neglected and (3.1) simplifies to

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] - \tau(\frac{1}{2}[H, \rho]_+ - \langle H \rangle \rho) \tag{3.11}$$

with

$$\tau = \beta\gamma. \tag{3.12}$$

Equation (3.7) for the derivative of the energy changes to

$$\frac{d}{d\tau}\langle H \rangle = \tau(\langle H^2 \rangle - \langle H \rangle^2) \tag{3.13}$$

which is negative or zero for positive β , i.e. the energy decreases.

Some important properties of the simplified evolution equation (3.11) are the following.

- (i) The equation is non-linear because of the term $\langle H \rangle$.
- (ii) Pure states remain pure. For

$$\rho = |\psi\rangle\langle\psi|. \tag{3.14}$$

Equation (3.10) can be rewritten as a non-linear Schrödinger equation

$$|\dot{\psi}\rangle = \frac{1}{i\hbar} H|\psi\rangle - \frac{1}{2}\tau(H - \langle H \rangle \mathbb{1})|\psi\rangle. \tag{3.15}$$

This non-linear evolution equation has been proposed and studied by Gisin in a series of articles (Gisin 1981a, b, 1982a, b, 1983a, b, 1986).

- (iii) For eigenstates of H , (3.15) reduces to the usual Schrödinger equation.

(iv) Stationary states ρ_n are the projectors on eigenstates of H , because stationarity implies $d\langle H \rangle/dt = 0$ and hence $\langle H^2 \rangle = \langle H \rangle^2$, which is satisfied iff $\rho = \rho_n = |n\rangle\langle n|$ with $H|n\rangle = \epsilon_n|n\rangle$. (We assume a discrete spectrum with $\epsilon_n < \epsilon_{n+1}$ for $n \geq 1$.)

(v) The stationary solutions ρ_n are unstable from below, i.e. any small admixture of a contribution from a lower state ρ_m ($m < n$) produces a time evolution towards ρ_m . The only stable state is the ground state.

Figure 5 illustrates the evolution equation (3.10) for the example of the three-state system discussed above. The eigenvalues ρ_n of ρ approach the asymptotic stable state (1, 0, 0). The other corners of the triangle, (0, 1, 0) and (0, 0, 1), are also stationary, however unstable. Comparison of figure 5 with the constant energy contours shown in figure 6 verifies the decrease of energy with time.

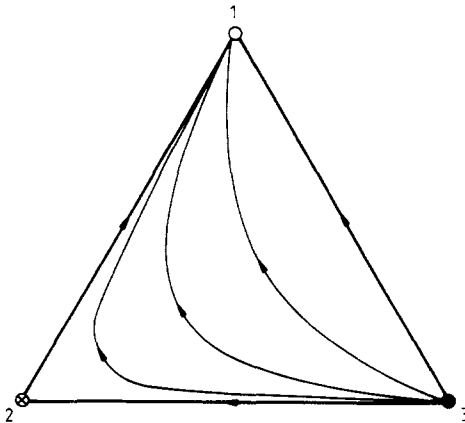


Figure 5. Phase portrait of a three-state system described by the simplified evolution equation (3.11). The energy is monotonically decreasing and the lowest state (○) is the stable asymptotic distribution.

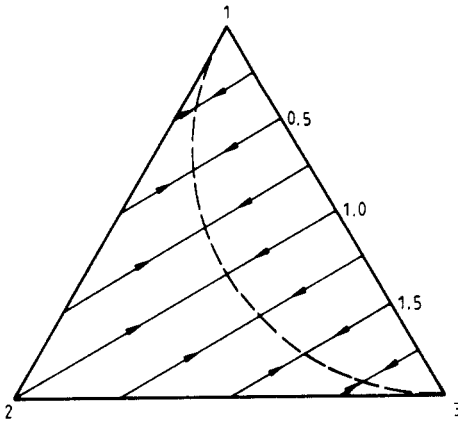


Figure 6. Phase portrait of a constrained three-state system described by (3.1), where β is given by (3.17). The energy $\langle H \rangle$ is kept constant in time and the entropy increases toward the constrained maximum of $\langle S \rangle$ on the broken curve, which gives the positions of the asymptotic equilibrium states, dependent on $\langle H \rangle$.

3.2. Constrained evolution

Under certain circumstances systems are restricted by constants. As an example we discuss the case where the free dissipative time evolution of a system is restricted by the condition that the mean energy of the system remains constant. In this case the parameter β in (3.1)—which acts as a kind of Lagrange parameter—is no longer constant. Its value is, however, given by the prescription

$$\langle H \rangle = \text{constant} \quad (3.16)$$

which can be rewritten as

$$\beta = \frac{\langle HS \rangle - \langle H \rangle \langle S \rangle}{\langle H^2 \rangle - \langle H \rangle^2} \quad (3.17)$$

by means of equation (3.7).

The evolution equation (3.1) with β given by (3.17) is identical with the equation recently designed and proposed by Beretta (Beretta *et al* 1984, 1985, Beretta 1985, 1986), who has also studied the mathematical properties of this equation and various applications. (Note, however, remark (e) in § 5 below concerning the interpretation of the evolution equations!) An important property is that the entropy is non-decreasing:

$$\frac{d}{dt} \langle S \rangle \geq 0. \quad (3.18)$$

A proof of (3.18) can be found in Beretta *et al* (1984, theorem 6) where a direct expression for $d\langle S \rangle/dt$ in terms of Gram determinants is also derived. The reader is referred to this work.

For the three-state system studied above the time evolution of the p_i follows the curves given by $\langle H \rangle = \text{constant}$, which are straight lines in the present case (see figure 6). During this process the entropy increases until the state reaches a relative maximum

of the entropy on this line. The position of these maxima can be obtained in closed form in this simple case and is given by

$$p_1 = \frac{1}{6}[1 + 3\langle H \rangle - (1 + 6\langle H \rangle - 3\langle H \rangle^2)^{1/2}]. \tag{3.19}$$

It is marked by a broken curve in figure 6.

4. Generalisations

The non-linear dissipative evolution equations proposed above can be easily generalised to the case where the coupling to the surrounding is generated by an arbitrary observable A instead of H , or—more generally—by various observables A_ν . Following Beretta (Beretta *et al* 1984, 1985, Beretta 1985, 1986) we call these A_ν the ‘generators of motion’. An example of such a set of A_ν is provided by $A_2 = H$, $A_3 = N$, which is a particle number operator. $\beta_2 = \beta = 1/kT$ is again the temperature parameter and $\beta_3 = -\beta\mu$ is proportional to the chemical potential μ .

Equation (3.1) generalises in this case to

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] - \gamma \sum_{\nu \geq 1} \beta_\nu (\frac{1}{2}[A_\nu, \rho]_+ - \langle A_\nu \rangle \rho) \tag{4.1}$$

with the identifications

$$A_1 = S \tag{4.2}$$

and

$$\beta_1 = -1. \tag{4.3}$$

The time dependence of expectation values (equation (3.6)) is generalised to

$$\frac{d}{dt}\langle B \rangle = \frac{1}{i\hbar}\langle [B, H] \rangle - \gamma \sum_{\nu} \beta_\nu (\frac{1}{2}\langle [B, A_\nu]_+ \rangle - \langle B \rangle \langle A_\nu \rangle). \tag{4.4}$$

In the case of a constrained time evolution, where the mean values $\langle A_\mu \rangle$ of some of the observables A_μ are constant—we assume that the A_ν are not explicitly time dependent—the parameters β_ν can be evaluated from (4.4): $d\langle A_\mu \rangle/dt = 0$ gives

$$\beta_\mu = \left(\frac{1}{i\hbar\gamma} \langle [A_\mu, H] \rangle + \sum_{\substack{\nu \geq 1 \\ \nu \neq \mu}} \beta_\nu (\frac{1}{2}\langle [A_\mu, A_\nu]_+ \rangle - \langle A_\mu \rangle \langle A_\nu \rangle) \right) (\langle A_\mu^2 \rangle - \langle A_\mu \rangle^2)^{-1} \tag{4.5}$$

which is the generalisation of (3.17) (note that $\langle HS \rangle = \langle SH \rangle$).

In some important cases the A_ν for $\nu \neq 1$ commute with each other and with the Hamiltonian H , which may be a member of the A_ν , of course. In this case the A_ν are said to be ‘in involution’. Then (4.5) simplifies to

$$\beta_\mu = \sum_{\substack{\nu \geq 1 \\ \nu \neq \mu}} \beta_\nu (\langle A_\mu A_\nu \rangle - \langle A_\mu \rangle \langle A_\nu \rangle) (\langle A_\mu^2 \rangle - \langle A_\mu \rangle^2)^{-1} \tag{4.6}$$

(note that $\langle A_\mu A_1 \rangle = \langle A_\mu S \rangle = \langle SA_\mu \rangle = \langle A_1 A_\mu \rangle$).

For a completely constrained system, where all the $\langle A_\mu \rangle$, $\mu \neq 1$, are held constant, (4.5) and (4.6) constitute a set of linear equations for the β_μ , which must be solved. In this case equation (4.1) turns out to be identical to the non-linear evolution equation proposed by Beretta (Beretta *et al* 1984, 1985, Beretta 1985, 1986), who has also shown that in this case the entropy is non-decreasing.

The generalised von Neumann equation (4.1) can be written in a notationally simpler form by introducing the identity as an additional observable

$$A_0 = \mathbb{1}. \quad (4.7)$$

Equation (4.1) is now

$$\dot{\rho} = \frac{1}{i\hbar} [H, \rho] - \gamma \sum_{\nu \geq 0} \frac{1}{2} \beta_\nu [A_\nu, \rho]_+ \quad (4.8)$$

and (4.4) is replaced by

$$\frac{d}{dt} \langle B \rangle = \frac{1}{i\hbar} \langle [B, H] \rangle - \gamma \sum_{\nu \geq 0} \frac{1}{2} \beta_\nu \langle [B, A_\nu]_+ \rangle + \left\langle \frac{\partial B}{\partial t} \right\rangle. \quad (4.9)$$

Conservation of probability $\text{Tr } \rho = \text{constant}$ gives the constraint

$$\langle A_0 \rangle = \text{constant} \quad (4.10)$$

which determines the value of β_0 . From (4.9) we obtain for $B = A_0$

$$\beta_0 = - \sum_{\nu \geq 1} \beta_\nu \langle A_\nu \rangle \quad (4.11)$$

or

$$\langle S \rangle = \beta_0 + \sum_{\nu \geq 0} \beta_\nu \langle A_\nu \rangle. \quad (4.12)$$

Inserting (4.11) into (4.8) we rediscover our previous equation (4.1).

Let us now look at stationary states for the case of a set of A_ν , which is in involution, i.e. $[H, A_\nu] = 0$, $[A_\nu, A_\mu] = 0$ for $\nu, \mu \neq 1$. The stationary state ρ_s will be a function of the A_ν , which commutes with all the A_ν and with H . $\dot{\rho}_s = 0$ in (4.8) then gives

$$\sum_{\nu \geq 0} \beta_\nu A_\nu \rho_s = 0. \quad (4.13)$$

If ρ_s is assumed to be invertible, this implies

$$\sum_{\nu \geq 0} \beta_\nu A_\nu = 0 \quad (4.14)$$

and therefore, with $A_1 = S = -\ln \rho_s$,

$$\rho_s = \exp \left(-\beta_0 \mathbb{1} - \sum_{\nu \geq 2} \beta_\nu A_\nu \right) \quad (4.15)$$

which is the well known generalised canonical distribution of quantum statistical mechanics. For the case $A_2 = H$, $A_3 = N$, ρ_s is the grand canonical distribution and

$$e^{\beta_0} = \text{Tr} \exp \left(- \sum_{\nu \geq 2} \beta_\nu A_\nu \right) \quad (4.16)$$

is the generalised partition function.

In addition to the stable equilibrium distribution (4.15) various unstable distributions are possible (ρ not invertible, i.e. ρ has zero eigenvalues), which are on the boundary of the state space, as discussed for the three-state system in § 3.

5. Concluding remarks

In the present paper we have proposed a novel equation for the time evolution of the density operator, which allows for a dissipative relaxation towards a steady-state distribution. The proposed generalised von Neumann equation is admittedly 'derived' heuristically. It has, however, an intrinsic simplicity which suggests that the equation may turn out to be a useful concept.

Of course, many things have still to be filled in, such as, for instance, the following.

(a) The existence and uniqueness of solutions.

(b) The physical relevance of the generators of motion.

(c) The derivation of the generalised von Neumann equation in the framework of subsystem dynamics.

(d) Application to interesting physical systems, as for instance the damped harmonic oscillator, spin relaxation and spin resonance.

(e) Last, but not least, it should be mentioned that the authors are aware of the fact that the proposed non-linear equation of motion for the density matrix is likely to induce conceptual and interpretational difficulties because the non-linear time evolution of the density operator is no longer compatible with the interpretation of the density operator as an incoherent mixture of pure states.

Work along these lines is necessary and currently in progress.

Appendix. Mixing enhancement

Let ρ and ρ' be two density matrices with eigenvalues p_i and p'_i , respectively, which are arranged in decreasing order.

$$\Sigma_k = \sum_{i=1}^k p_i \quad \Sigma'_k = \sum_{i=1}^k p'_i \tag{A1}$$

are the partial sums. We call ρ' more mixed than ρ if

$$\Sigma'_k \leq \Sigma_k \quad k = 1, \dots, n \tag{A2}$$

and a time evolution $t \rightarrow t'$ is said to be mixing enhancing if $\rho(t')$ is more mixed than $\rho(t)$. ρ' more mixed than ρ implies $S(\rho') \geq S(\rho)$, i.e. mixing enhancement is a stronger property than entropy production. Further properties of the concept of mixing enhancement are discussed in Wehrl's review article on properties of entropy (Wehrl 1978).

The free dissipation (2.12) is mixing enhancing because

$$\dot{p}_i = -\gamma(\ln p_i + \langle S \rangle) p_i \tag{A3}$$

(equation (2.30)) implies

$$\frac{d}{dt} \Sigma_k = \sum_{i=1}^k \dot{p}_i = -\gamma \Sigma_k (\langle S \rangle - S_k / \Sigma_k) \tag{A4}$$

with

$$S_k = -\sum_{i=1}^k p_i \ln p_i. \tag{A5}$$

The expression

$$\rho_k = S_k / \Sigma_k \tag{A6}$$

is monotonically increasing with k . The monotonicity of the p_i ($p_i \geq p_{k+1}$, $i \leq k+1$) implies

$$\sum_{i=1}^k p_i \ln \frac{p_i}{p_{k+1}} \geq 0 \quad (\text{A7})$$

and therefore

$$-\sum_{i=1}^k p_i \ln p_{k+1} \geq -\sum_{i=1}^k p_i \ln p_i \quad (\text{A8})$$

which can be rewritten as

$$-\ln p_{k+1} \geq \varphi_k. \quad (\text{A9})$$

Multiplying with p_{k+1}/Σ_k and adding φ_k on both sides we have

$$\varphi_k - \frac{p_{k+1}}{\Sigma_k} \ln p_{k+1} \geq \varphi_k + \frac{p_{k+1}}{\Sigma_k} \varphi_k \quad (\text{A10})$$

or

$$\varphi_k \leq \frac{\varphi_k - (p_{k+1}/\Sigma_k) \ln p_{k+1}}{1 + p_{k+1}/\Sigma_k} = \varphi_{k+1}. \quad (\text{A11})$$

We therefore have

$$0 \leq \frac{S_k}{\Sigma_k} \leq \frac{S_{k+1}}{\Sigma_{k+1}} \leq \langle S \rangle. \quad (\text{A12})$$

Finally we see from (A4) and (A12)

$$\frac{d}{dt} \Sigma_k \leq 0 \quad (\text{A13})$$

i.e. the time evolution is mixing enhancing.

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