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Approximate master equations for an exactly solvable quantum system

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Abstract. Approximate master equations for the Friedrichs model are discussed. The approximate Zwanzig equation predicts behaviour very close to the exact one, but presents only minor simplifications of necessary calculations, while an approximate convolutionless equation usually gives a reasonably good account of the behaviour of exact solutions and simplifies the calculations significantly. It is also shown that the van Hove and Markov limits give an incorrect asymptotics in a physically interesting case.

1. Introduction

Equations obtained from the Liouville-von Neumann equation

$$d_t\rho(t) = -iL\rho(t) = -i[H, \rho(t)] \tag{1.1}$$

where $\rho(t)$ is the density operator of a given physical system, H its Hamiltonian and L the corresponding Liouvillean (d_t stands for the derivative with respect to time, and we assume thoroughout this paper that $h/2\pi = 1$), by splitting the density operator into 'relevant' and 'irrelevant' parts by means of a projection superoperator D

$$\begin{aligned} \rho_d(t) &= D\rho(t) \\ \rho_{nd}(t) &= (1-D)\rho(t) \end{aligned} \tag{1.2}$$

are called exact master equations. They describe the time evolution of the 'relevant' part $\rho_d(t)$, and thus provide another theoretical description of the dynamics of quantum systems. However, they also serve as a starting point for the derivation of many approximate equations, which in turn act as powerful tools in a variety of calculations. The purpose of the present paper is to introduce some approximate (in the sense of the weak coupling limit) master equations for a simple and well understood quantum model, namely that of Friedrichs 1948, and to compare the results obtained with exact solutions, or with solutions obtained in different ways. We hope that such an analysis will in future encourage making similar approximations while solving more complicated problems.

There are several types of exact master equations. An equation with a convolution was introduced by Zwanzig (1960) and independently by the Brussels school (Résibois 1963), and since then it has been used by many authors with considerable success.

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The equation is usually solved in the so-called Markov limit (see e.g. Haake 1973, Agarwal 1974). Although some rigorous criteria for the existence of Markovian approximations of non-Markovian dynamical equations have been formulated (see e.g. Spohn 1980), only rarely do they appear to be checked by authors, who usually assume that only some qualitative ones, like for instance the assumption that relaxation times of a thermal bath are much smaller than those of a 'relevant' subsystem, are satisfied. Perhaps as a consequence of this practice, or as a consequence of the extreme complexity of the Zwanzig equation without a Markovian approximation that makes it almost impossible to perform any calculations even in the lowest-order approximation, the Markov limit is taken almost whenever a master equation with a convolution is being used. However, it has been already reported (e.g. Čapek 1983) that in this limit the equation predicts an incorrect long-time asymptotics, and we give further evidence on this point in the present paper. There are also exact master equations without a convolution. These are usually valid if and only if certain superoperators can be proved to exist. In this paper we use a formalism introduced by Fuliński (1967), or rather its simplest form (Fuliński and Kramarczyk 1968). Perhaps another convolutionless formalism, namely that of the 'memory effect renormalisation' (Hashitsume *et al* 1977), is more popular, but it has been shown to be equivalent to the one we use (Gzyl 1981), though their asymptotic properties might be different.

Master equations have been frequently associated with the famous van Hove limit (van Hove 1955; see also Loss (1986) for further bibliography and a comprehensive discussion), another procedure leading to weak coupling approximations. Yet it has been recently shown (Braun and Mello 1986), in a slightly different context, that this limit may obscure some important features of the dynamics of a physical system. We find some more evidence on this point as well.

In § 2 we present a convolutionless master equation for the Friedrichs model, and then we introduce an approximate form of the equation. In § 3 we do the same with an equation with a convolution. In subsequent sections we present some model calculations, rather trivial in § 4, and more elaborate and perhaps more interesting, because they concern a physically important case of photodissociation, in § 5. We draw our final conclusions in § 6.

2. Convolutionless master equation

In the present paper we use an exact convolutionless master equation which has been derived under the assumptions that both the Hamiltonian H and the projector D are time independent. The equation is (Fuliński and Kramarczyk 1968)

$$\mathrm{d}_t\rho_d(t) = [\mathrm{d}_t N(t, t_0)]N^{-1}(t, t_0)[\rho_d(t) + \rho_{nd}(t_0)] \tag{2.1}$$

where

$$N(t, t_0) = 1 + D[Z(t, t_0) - 1]. \tag{2.2}$$

D is the projector (1.2), $Z(t, t_0)$ is the time evolution superoperator

$$Z(t_1, t_2)\rho(t_3) = \rho(t_1 + t_3 - t_2) \tag{2.3}$$

and t_0 is an arbitrarily chosen moment of preparation of the system. The inverse superoperator N^{-1} exists if and only if the condition

$$\lim_{n\to\infty} [1 - N(t, t_0)]^n = 0 \tag{2.4}$$

holds in some sense and, if this is the case,

$$N^{-1}(t, t_0) = \sum_{k=0}^{\infty} [D - DZ(t, t_0)]^k. \tag{2.5}$$

The continuous version of the Friedrichs Hamiltonian is

$$H = \varepsilon_\phi |\phi\rangle\langle\phi| + \int \omega |\omega\rangle\langle\omega| \mathrm{d}\omega + \lambda \int [V(\omega)|\phi\rangle\langle\omega| + V^*(\omega)|\omega\rangle\langle\phi|] \mathrm{d}\omega \tag{2.6}$$

and both the orthonormality and the completeness of the basis are customarily assumed. $|\phi\rangle$ can be interpreted as the upper state of a two-level atom, while $|\omega\rangle$ are the states of a 'bosonic' field (namely photons or phonons) that the atom interacts with, λ being the coupling constant. It is natural to choose the state $|\phi\rangle$ as the 'relevant' part of the system (i.e. associated with the macroscopically relevant information about the system), and we put

$$D\rho(t) = \rho_d(t) = \rho_{\phi\phi}(t)|\phi\rangle\langle\phi| = p_\phi(t)|\phi\rangle\langle\phi|. \tag{2.7}$$

$p_\phi(t)$ is the probability that the state $|\phi\rangle$ is being occupied. The condition (2.4) can be now interpreted as

$$\lim_{n\to\infty} [1 - N(t, t_0)]^n |\phi\rangle\langle\phi| = 0. \tag{2.8}$$

Because for any operator A

$$Z(t, t_0)A = U(t - t_0) A U^\dagger(t - t_0) \tag{2.9}$$

where

$$U(\tau) = \exp(-\mathrm{i}\tau H) \tag{2.10}$$

is the evolution superoperator and $U^\dagger$ stands for its Hermitian conjugate, after some simple algebra one can obtain that

$$D(Z-1)|\phi\rangle\langle\phi| = [|U_{\phi\phi}(t - t_0)|^2 - 1]|\phi\rangle\langle\phi| \tag{2.11}$$

and the condition (2.8) is obviously satisfied. The explicit form of the equation (2.1) for the Friedrichs model can now be straightforwardly derived, but for the sake of simplicity we impose the spontaneous emission initial conditions

$$p_\phi(0) = 1 \qquad \rho_{nd}(0) = 0 \tag{2.12}$$

under which the inhomogeneous term in (2.1) vanishes. From (2.5) and (2.11) we now have (hereafter we put $t_0 = 0$ for simplicity)

$$N^{-1}|\phi\rangle\langle\phi| = |U_{\phi\phi}|^{-1}|\phi\rangle\langle\phi|. \tag{2.13}$$

The superoperator Z itself satisfies the Liouville-von Neumann equation

$$\mathrm{d}_t Z(t, t_0) = -\mathrm{i} L Z(t, t_0) \tag{2.14}$$

and from the definition (2.2) we now have that

$$\mathrm{d}_t N(t, t_0) = -\mathrm{i} D L Z(t, t_0). \tag{2.15}$$

It can now be shown by some elementary, though rather lengthy calculations, that

$$\mathrm{d}_t N|\phi\rangle\langle\phi| = -\mathrm{i}\lambda \int \mathrm{d}\xi [V(\xi) U_{\xi\phi} U^\dagger_{\phi\phi} - V^*(\xi) U_{\phi\phi} U^\dagger_{\phi\xi}]|\phi\rangle\langle\phi|. \tag{2.16}$$

Putting the results together we arrive, after some more algebra, at the conclusion that

$$\mathrm{d}_t p_\phi(t) = B(t) p_\phi(t) \tag{2.17}$$

where

$$B(t) = -\mathrm{i}\lambda \int \mathrm{d}\xi [V(\xi) U_{\xi\phi} (U_{\xi\xi})^{-1} - V^*(\xi) U^\dagger_{\phi\xi} (U^\dagger_{\xi\xi})^{-1}]. \tag{2.18}$$

Note that (2.17) is a number equation. This comes as a consequence of the fact that the projectors $|\phi\rangle\langle\phi|$, being the only remaining operators in the resulting master equation, have been dropped. It is also a matter of simple algebra to check that

$$p_\phi(t) = |U_{\phi\phi}|^2 \tag{2.19}$$

is the formal solution of (2.17), as one may have expected.

So, as one can easily see, the forms of both the equation (2.17) and its solution (2.19) depend on matrix elements of U. Only on rare occasions can these be obtained from the definition (2.10), and one rather calculates them from the equation

$$\mathrm{d}_t U(t) = -\mathrm{i} H U(t) \tag{2.20}$$

which in the present case splits into the following set of equations:

$$\mathrm{d}_t U_{\phi\phi} = -\mathrm{i}\varepsilon_\phi U_{\phi\phi} - \mathrm{i}\lambda \int \mathrm{d}\xi \, V(\xi) U_{\xi\phi} \tag{2.20a}$$

$$\mathrm{d}_t U_{\omega\phi} = -\mathrm{i}\omega U_{\omega\phi} - \mathrm{i}\lambda V^*(\omega) U_{\phi\phi} \tag{2.20b}$$

which can be solved by means of the Laplace transformation. For the transforms we get

$$\tilde{U}_{\phi\phi}(s) = \left(s + \mathrm{i}\varepsilon_\phi + \lambda^2 \int \mathrm{d}\xi |V(\xi)|^2 (s + \mathrm{i}\xi)^{-1} \right)^{-1} \tag{2.21a}$$

$$\tilde{U}_{\omega\xi}(s) = -\mathrm{i}\lambda V^*(\omega)(s + \mathrm{i}\omega)^{-1} \tilde{U}_{\phi\phi}(s). \tag{2.21b}$$

The above equations enable us to find the exact solution (2.19) (provided that the transformation can be inverted), but they also can serve as a starting point for obtaining a perturbation expansion of (2.17). In the present paper, for reasons to be explained below, we restrict ourselves to the lowest-order approximation, but the procedure we propose can be carried on further and can give an approximation of any order required.

If λ is sufficiently small, the transforms (2.21) can be expanded as power series in λ. If we keep only the least non-vanishing terms, we get

$$U_{\phi\phi}(t) = \exp(-\mathrm{i}\varepsilon_\phi t) + \mathrm{O}(\lambda^2) \tag{2.22a}$$

$$U_{\omega\phi}(t) = \lambda V^*(\omega)[\exp(-\mathrm{i}\omega t) - \exp(-\mathrm{i}\varepsilon_\phi t)](\omega - \varepsilon_\phi)^{-1} + \mathrm{O}(\lambda^3) \tag{2.22b}$$

where the transforms have been formally inverted. From (2.17) and (2.18) we now get

$$\mathrm{d}_t p_\phi(t) = -2\lambda^2 \int \mathrm{d}\omega |V(\omega)|^2 \sin[(\omega - \varepsilon_\phi)t](\omega - \varepsilon_\phi)^{-1} p_\phi(t) \tag{2.23}$$

or

$$p_\phi(t) = \exp\left(-2\lambda^2 \int \mathrm{d}\omega |V(\omega)|^2 \{1 - \cos[(\omega - \varepsilon_\phi)t]\}(\omega - \varepsilon_\phi)^{-2} \right). \tag{2.24}$$

It is conceivable that the (approximate) behaviour of $p_\phi(t)$ can be estimated from (2.23) or (2.24) even when the (exact) transforms (2.21) cannot be inverted. We shall see in §§ 4 and 5 that this approximation usually predicts a correct asymptotics of systems under consideration.

It is also a matter of simple algebra to show that instead of (2.21) we can put

$$\mathrm{d}_t x(t) = -\lambda^2 \int \mathrm{d}\omega |V(\omega)|^2 \int_0^t \mathrm{d}t'\, x(t') \exp[-\mathrm{i}(\omega - \varepsilon_\phi)(t-t')] \tag{2.25}$$

where

$$x(t) = \exp(\mathrm{i}\varepsilon_\phi t) U_{\phi\phi}(t). \tag{2.26}$$

Note that

$$p_\phi(t) = |U_{\phi\phi}(t)|^2 = |x(t)|^2 \tag{2.27}$$

and that $x(0) = 1$.

3. The Zwanzig method

Now we switch to equations with a convolution, or as it is commonly called, with memory. We use here the Zwanzig equation (Zwanzig 1960)

$$\mathrm{d}_t \rho_d(t) = -\mathrm{i}DL\rho_d(t) - \mathrm{i}DL \exp[-\mathrm{i}t(1-D)L]\rho_{nd}(t_0) - \int_0^t \mathrm{d}t'\, DL \exp[-\mathrm{i}t'(1-D)L](1-D)L\rho_d(t-t'). \tag{3.1}$$

For the Friedrichs model with the projector D defined by (2.7), and with the initial conditions (2.12) imposed, the second term in the equation vanishes and we have

$$\mathrm{d}_t p_\phi(t)|\phi\rangle\langle\phi| = -\mathrm{i}p_\phi(t) DL|\phi\rangle\langle\phi| - \int_0^t \mathrm{d}t' p_\phi(t-t') DL \exp[-\mathrm{i}t'(1-D)L](1-D)L|\phi\rangle\langle\phi|. \tag{3.2}$$

Let us define (A being an operator)

$$L_S A = \varepsilon_\phi [|\phi\rangle\langle\phi|, A] \tag{3.3a}$$

$$L_B A = \int \omega[|\omega\rangle\langle\omega|, A]\, \mathrm{d}\omega \tag{3.3b}$$

$$L_{SB} A = \int \mathrm{d}\omega [V(\omega)|\phi\rangle\langle\omega| + V^*(\omega)|\omega\rangle\langle\phi|, A]\, \mathrm{d}\omega. \tag{3.3c}$$

Now

$$L = L_S + L_B + \lambda L_{SB}. \tag{3.4}$$

It is easy to check that these superoperators satisfy the following Zwanzig identities:

$$DLD = 0 \tag{3.5a}$$

$$DL_S = L_S D = 0 \tag{3.5b}$$

$$DL_B = L_B D = 0. \tag{3.5c}$$

The first of these identities causes the first term in (3.2) to vanish, while the other two enable us to simplify the only lasting (and most complicated) term. After some algebra we obtain that

$$\mathrm{d}_t p_\phi(t)|\phi\rangle\langle\phi| = -\lambda^2 \int_0^t \mathrm{d}t'\, p_\phi(t-t') D L_{SB} \exp[-\mathrm{i}t'(1-D)L] \times \int \mathrm{d}\omega [V^*(\omega)|\omega\rangle\langle\phi| - V(\omega)|\phi\rangle\langle\omega|]. \tag{3.6}$$

Equation (3.6) is still exact. Note that further calculations with the full superoperator

$$\exp[-\mathrm{i}t(1-D)L] \tag{3.7}$$

would probably be extremely difficult, and that (3.6) is at least second order in λ. The approximation we are going to apply reduces to replacing (3.7) by

$$\exp[-\mathrm{i}t(1-D)(L_S+L_B)] = \exp[-\mathrm{i}t(L_S+L_B)]. \tag{3.8}$$

A similar procedure was first carried out by Zwanzig (1964), who has also pointed out that any calculations in higher than second order of perturbation expansion of (3.1) would most probably be as complicated as solving the exact equation. For that reason and because we aim at comparing different types of formalisms, we have restricted ourselves to the second-order approximation in the previous section.

Now we can express the exponent as a power series and interchange the order of summation and integration over ω. Because

$$(L_S L_B - L_B L_S)|\phi\rangle\langle\omega| = 0 \tag{3.9}$$

$$(L_S L_B - L_B L_S)|\omega\rangle\langle\phi| = 0 \tag{3.10}$$

we can use the Newton rule to compute expressions $(L_S+L_B)^n|\phi\rangle\langle\omega|$ and $(L_S+L_B)^n|\omega\rangle\langle\phi|$, and finally after some more algebra we obtain that

$$\mathrm{d}_t p_\phi(t)|\phi\rangle\langle\phi| = -2\lambda^2 \int_0^t \mathrm{d}t'\, p_\phi(t-t') \int \mathrm{d}\omega |V(\omega)|^2 \cos[(\omega-\varepsilon_\phi)t']|\phi\rangle\langle\phi|. \tag{3.11}$$

Because the projectors $|\phi\rangle\langle\phi|$ are the only operators that appear in (3.11), we again can drop them and arrive at

$$\mathrm{d}_t p_\phi(t) = -2\lambda^2 \int_0^t \mathrm{d}t'\, p_\phi(t-t') \int \mathrm{d}\omega |V(\omega)|^2 \cos[(\omega-\varepsilon_\phi)t'] \tag{3.12}$$

which is again a number equation.

Equation (3.12) resembles (2.25) very much. If we could interchange the order of integrations—and the uniform convergence of

$$\int \mathrm{d}\omega |V(\omega)|^2 \cos[(\omega-\varepsilon_\phi)t] \tag{3.13}$$

is sufficient for the legitimacy of such a procedure—the resemblance would be even more apparent. Both (2.25) and (3.12) are integro-differential equations, and the kernel of the latter is equal to the real part of that of the former, times two (note that $p_\phi(t)$ must be real while $x(t)$ can be complex). It means that the approximate $p_\phi(t)$ obtained from (3.12) should be very close to the exact one, but it also means that the second-order Zwanzig approximation provides only minor simplifications to the calculations, and it is very likely that one may face the same difficulties while solving either of the two equations.

If the integral (3.13) actually uniformly converges, we can make a further approximation, namely to neglect the t' dependence of p_ϕ in (3.12). If we do this, we again obtain (2.23), i.e. the convolutionless master equation in the second-order approximation. Thus it looks as if the approximate Zwanzig equation were 'less approximate' than the approximate convolutionless one.

4. Simple examples

The two examples we are going to give in this section are rather artificial and unsophisticated, but we think one may still learn some interesting features from them. As one can see, the potential function $V(\omega)$, or rather its square modulus, is what has to be specified, along with the spectrum of $|\omega\rangle$. Let us assume that

$$|V(\omega)|^2 = (\gamma/\pi)[(\omega-\varepsilon_\phi)^2+\gamma^2]^{-1} \tag{4.1}$$

and that $\omega \in (-\infty, +\infty)$. The exact solution (2.19) now becomes

$$p_\phi(t) = \exp(-\gamma t)[\cosh(at)+(\gamma/2a)\sinh(at)]^2 \tag{4.2}$$

where

$$a^2 = \tfrac{1}{4}\gamma^2 - \lambda^2. \tag{4.3}$$

This, but not the subsequent approximate solutions, may be treated merely as a quotation, because this particular example has been already examined by many authors (Middleton and Schieve 1973, Frankowicz and Jędrzejek 1978). Now let us examine various approximations.

The solution of the approximate convolutionless equation is

$$p_\phi(t) = \exp(-2\lambda^2\gamma^{-1}t)\exp\{2(\lambda/\gamma)^2[1-\exp(-\gamma t)]\} \tag{4.4}$$

and the approximate Zwanzig equation

$$\mathrm{d}_t p_\phi(t) = -2\lambda^2\int_0^t \mathrm{d}t'\, p_\phi(t-t')\exp(-\gamma t') \tag{4.5}$$

leads to

$$p_\phi(t) = \exp(-\gamma t)[\cosh(bt)+(\gamma/2b)\sinh(bt)] \tag{4.6}$$

where

$$b^2 = \tfrac{1}{4}\gamma^2 - 2\lambda^2. \tag{4.7}$$

It is also easy to check both the Markov limit of (4.4) and the van Hove limit

$$\lambda \to 0,\ t\to\infty \text{ such that } \lambda^2 t = \text{fixed} \tag{4.8}$$

of any of the above solutions give

$$p_\phi(t) = \exp(-2\lambda^2\gamma^{-1}t). \tag{4.9}$$

We can see that all of these solutions describe very similar behaviours of the probability $p_\phi(t)$ and that the approximate Zwanzig solution (4.6) is indeed very close to the solution (4.2), the exact one, not only in form, but also in characteristic features: even when the exact solution starts to exhibit damped oscillations for values of λ greater than $\frac{1}{2}\gamma$, the approximate solution does the same, though for slightly greater values of λ, while one might have expected the approximation to break down completely for such large values of the coupling constant. The approximate convolutionless solution (4.3) provides a very good account of the behaviour of the actual solution (4.2) for small values of λ, and the Markov (or van Hove, because in this case they lead to the same result) limit, though coarse grained, still gives a fairly good long-time asymptotics.

We have not managed to find the exact solution in our second example, but nevertheless we give it because it can remind our reader—and ourselves, too—that not all approximations work well.

We put

$$|V(\omega)|^2=(\pi\tau)^{-1}\{1-\cos[(\omega-\varepsilon_\phi)\tau]\}(\omega-\varepsilon_\phi)^{-2} \tag{4.10}$$

and again $\omega\in(-\infty,+\infty)$. Equation (2.25) now becomes

$$\mathrm{d}_t x(t)=-\lambda^2\tau^{-1}\int_0^t \mathrm{d}t'\, x(t-t')(\tau-t')\theta(\tau-t') \tag{4.11}$$

where θ is the Heaviside step function. For the Laplace transform of $x(t)$ we obtain

$$\tilde{x}(s)=s^2\{s^3+a^2[s+\exp(-s)-1]\}^{-1} \tag{4.12}$$

where we have decided to measure time in the units of τ, and

$$a=\lambda\tau \tag{4.13}$$

is a dimensionless constant. It is easy to check that $s=0$ is the only real zero of the denominator on the right-hand side of (4.12).

The approximate Zwanzig equation leads to

$$\tilde{p}_\phi(s)=s^2\{s^3+2a^2[s+\exp(-s)-1]\}^{-1}. \tag{4.14}$$

As we have mentioned, we have not managed to invert these transforms. Note, however, that if $a=2k\pi$ (k being an integer), the right-hand side of (4.12) has simple poles at points $s=\pm 2k\pi\mathrm{i}$, and hence the solution (at least asymptotically) behaves periodically. The approximate Zwanzig solution exhibits an analogous feature. On the contrary, the solution of the approximate convolutionless equation for the potential (4.10) is (t still in units of τ)

$$p_\phi(t)=\exp(\tfrac{1}{3}a^2 d(t)) \tag{4.15}$$

where

$$d(t)=3t^2-t^3 \qquad \text{for } 0\leqslant t\leqslant 1 \tag{4.16a}$$

$$d(t)=3t-1 \qquad \text{for } t>1 \tag{4.16b}$$

and $p_\phi(t)$ tends to zero monotonically. One must then remember that some important effects may not be observed if a problem is solved with the aid of an approximate master equation (note though that $\lambda=2\pi/\tau$ hardly can be regarded as a small number).

5. Another example: photodissociation

Our final example is perhaps more interesting than the previous two because it has something in common with a situation that can be observed in a possible experiment.

As is widely known, photodetachment of electrons from negative ions can be described within the framework of the Friedrichs model, provided that $|V(\omega)|^2$ behaves like $\omega^{L+1/2}$, where L is the angular momentum of continuum (Wigner 1948). We choose the s wave and put

$$|V(\omega)|^2 = \pi^{-1}[\beta(\omega - \varepsilon_\phi)]^{1/2}(\omega - \varepsilon_\phi + \beta)^{-1} \tag{5.1}$$

and we assume that $\omega \in [\varepsilon_\phi, +\infty)$. It is because this particular model has already been investigated (Rzążewski *et al* 1982) that we have chosen it: this provides us with an opportunity to test our formalism in a case where an exact solution is already known and which belongs to a class of a great interest. (We must admit though that our model is slightly simplified, and consequently we discuss not a genuine photodetachment, but rather a spontaneous emission with the interaction (5.1).)

The exact solution satisfies the equation

$$\mathrm{d}_t x(t) = -\lambda^2\pi^{-1}\int_{\varepsilon_\phi}^{\infty} \mathrm{d}\omega[\beta(\omega - \varepsilon_\phi)]^{1/2}(\omega - \varepsilon_\phi + \beta)^{-1} \times \int_0^t \mathrm{d}t' x(t-t') \exp[-\mathrm{i}(\omega - \varepsilon_\phi)t']. \tag{5.2}$$

If we decide to measure time in units of β^{-1}, and appropriate change of variables leads to

$$\mathrm{d}_t x(t) = -w\pi^{-1}\int_0^t \mathrm{d}t'\, x(t-t') \int_0^\infty z^{1/2}(1+z)^{-1}\exp(-\mathrm{i}t'z)\,\mathrm{d}z \tag{5.3}$$

where

$$w = \lambda^2\beta^{-1} \tag{5.4}$$

is an effective coupling constant. The integral over z can be carried out explicitly (Gradshteyn and Ryzhik 1980). We get

$$\mathrm{d}_t x(t) = -\tfrac{1}{2}w\pi^{-1/2}\int_0^t \mathrm{d}t'\, x(t-t')\exp(-\mathrm{i}t')\Gamma(-\tfrac{1}{2}, -\mathrm{i}t') \tag{5.5}$$

where $\Gamma(a, b)$ denotes the incomplete gamma function (Erdélyi *et al* 1953). For the Laplace transform of x we get (Erdélyi *et al* 1954)

$$\tilde{x}(s) = (s^{1/2} + (-\mathrm{i})^{1/2})[s(s^{1/2} + (-\mathrm{i})^{1/2}) + \mathrm{i}^{1/2}w]^{-1} \tag{5.6}$$

and finally (Erdélyi *et al* 1954)

$$x(t) = \tfrac{1}{2}\pi^{-1/2}\sum_{j=1}^{3} c_j \int_0^\infty u\exp[-u^2/(4t)]\exp(y_j u)\,\mathrm{d}u \tag{5.7}$$

where y_j are poles of the function

$$h(z) = (z + (-\mathrm{i})^{1/2})[z^2(z + (-\mathrm{i})^{1/2}) + \mathrm{i}^{1/2}w]^{-1} \tag{5.8}$$

and c_j are the corresponding residua. After some simple algebra, (5.7) becomes

$$x(t) = \tfrac{1}{2}\pi^{-1/2}\sum_{j=1}^{3} c_j y_j \exp(y_j^2 t)\,\mathrm{erfc}(-y_j t^{1/2}) \tag{5.9}$$

where $\mathrm{erfc}(a)$ means the complex error function (Erdélyi *et al* 1953). From the asymptotic properties of this function one can see that the decay of the bound state $|\phi\rangle$ is essentially non-exponential. Actually, the leading term in $p_\phi(t)$ is proportional to t^{-3}.

These results are in full accordance with those of Rzążewski and his collaborators. Now let us see what the approximate solutions look like.

The approximate Zwanzig equation in the present case is

$$\mathrm{d}_t p_\phi(t) = -\tfrac{1}{2} w \pi^{-1/2} \int_0^t \mathrm{d}t' \, p_\phi(t-t') \times [\exp(\mathrm{i}t')\Gamma(-\tfrac{1}{2}, \mathrm{i}t') + \exp(-\mathrm{i}t')\Gamma(-\tfrac{1}{2}, -\mathrm{i}t')]. \tag{5.10}$$

This equation also can be solved by means of the Laplace transformation, and its solution has the general form of (5.9) with the only difference, apart from that of different coefficients, being that the solution of (5.10) is a sum of four, instead of three, terms proportional to $\operatorname{erfc}(-\text{constant} \times t^{1/2})$. Obviously, this would give the same asymptotics as the exact solutions.

Let us, however, look at the Markov limit of (5.10). The formal expression for the limit has the form

$$\mathrm{d}_t p_\phi(t) = -\tfrac{1}{2} w \pi^{-1/2} p_\phi(t) \lim_{t \to \infty} f(t) \tag{5.11}$$

where

$$f(t) = \int_0^t \mathrm{d}t' [\exp(\mathrm{i}t')\Gamma(-\tfrac{1}{2}, \mathrm{i}t') + \exp(-\mathrm{i}t')\Gamma(-\tfrac{1}{2}, -\mathrm{i}t')]. \tag{5.12}$$

The Laplace transform of this function is (Erdélyi *et al* 1954)

$$\tilde{f}(s) = 2^{3/2} \pi s^{-1/2} (s^2+1)^{-1} [s - (2s)^{1/2} + 1] \tag{5.13}$$

and hence

$$f(t) = 2^{1/2} t^{-3/2} \int_0^\infty \mathrm{d}u \, u \exp[-u^2/(4t)] \times \{1 - \exp(-2^{-1/2}u)[\cos(2^{-1/2}u) + \sin(2^{-1/2}u]\}. \tag{5.14}$$

It is apparent that the term proportional to $\exp(-2^{-1/2}u)$ tends to zero as t goes to infinity, while the other one diverges like $t^{1/2}$. Hence we can say that the Markov limit of the Zwanzig equation gives asymptotically

$$p_\phi(t) = \exp[-w(2\pi)^{-1/2} t^{3/2}]. \tag{5.15}$$

This asymptotics is obviously incorrect.

Now let us turn to the approximate convolutionless equation. Its formal solution (2.24) now becomes

$$p_\phi(t) = \exp\left(-2w\pi^{-1} \int_0^t \mathrm{d}t' \int_0^\infty \mathrm{d}z \sin(t'z) z^{-1/2} (1+z)^{-1}\right) \tag{5.16}$$

or

$$p_\phi(t) = \exp\left(-\mathrm{i}w\pi^{-1} \int_0^t \mathrm{d}t' [\exp(-\mathrm{i}t')\Gamma(\tfrac{1}{2}, -\mathrm{i}t') - \exp(\mathrm{i}t')\Gamma(\tfrac{1}{2}, \mathrm{i}t')]\right). \tag{5.17}$$

The exponent in (5.17) has a most difficult form, and any properties of $p_\phi(t)$ can be obtained from (5.17) only numerically. But we shall follow another way. Equation (5.16) is equivalent to

$$p_\phi(t)=\exp\left(-4w\pi^{-1}\int_0^t \mathrm{d}t'\int_0^\infty \mathrm{d}z\,\sin(t'z^2)(1+z^2)^{-1}\right). \tag{5.18}$$

The innermost integral in (5.18) can, by a simple contour integration, be converted into

$$\int_0^\infty \mathrm{d}z\,\sin(t'z^2)(1+z^2)^{-1}=2^{-1/2}\int_0^\infty \mathrm{d}z(1-z^2)\exp(-t'z^2)(1+z^4)^{-1} \tag{5.19}$$

and (5.18) now becomes

$$p_\phi(t)=\exp\left(-2^{3/2}w\pi^{-1}\int_0^\infty \mathrm{d}z(1-z^2)[1-\exp(-tz^2)](1+z^4)^{-1}z^{-2}\right) \tag{5.20}$$

which corresponds to

$$\mathrm{d}_t p_\phi(t)=-2^{3/2}w\pi^{-1}\int_0^\infty \mathrm{d}z(1-z^2)\exp(-tz^2)(1+z^4)^{-1}p_\phi(t). \tag{5.21}$$

Note that for small z

$$z^{-2}[1-\exp(-tz^2)]\sim t \tag{5.22}$$

and the integrand in (5.20) diverges for $t\to\infty$. Because

$$\int_0^\infty \mathrm{d}z(1-z^2)\exp(-tz^2)(1+z^4)^{-1}=2^{-1/2}\int_1^\infty \mathrm{d}u\,u^{-1}\exp(-ut)\sinh[t(2u-1)^{1/2}] \tag{5.23}$$

which is greater than zero for all $t>0$, we can conclude that $p_\phi(t)$ tends to zero monotonically as t goes to infinity.

Note also that in this case the van Hove limit makes no sense, because in this limit

$$p_\phi(t)=\exp\left(-2^{3/2}w\pi^{-1}\int_0^\infty \mathrm{d}z(1-z^2)(1+z^4)^{-1}\right) \tag{5.24}$$

but the integral in the above expression vanishes, and $p_\phi(t)$ turns out to be identically equal to one, which is unphysical. This may indicate a non-exponential behaviour of the approximate probability $p_\phi(t)$ (of course we already know that the exact $p_\phi(t)$ does behave non-exponentially). Indeed, one can easily check that for any positive constant α

$$\lim_{t\to\infty}[p_\phi(t)/\exp(-\alpha t)]=\infty \tag{5.25}$$

where $p_\phi(t)$ is given by any of the (equivalent) expressions (5.16), (5.17), (5.18) or (5.20). That means that any exponential function tends to zero faster that the solution of the approximate convolutionless master equation (5.21).

We have seen that the exact convolutionless equation gives results identical to those obtained in a different way, and that the approximate Zwanzig equation gives results very close to the exact solution. The approximate convolutionless equation enables us to predict the asymptotic behaviour of the exact solution, too, though these predictions are not as good as those obtained from the approximate equation with a convolution. Unlikely in our first example, the Markov and van Hove limits give evidently incorrect long-time asymptotics.

6. Conclusions

We think that the following 'hierarchy' of solutions of different master equations can be established.

(i) The exact solution (2.19) of the exact convolutionless equation (2.17); to obtain this one has to solve (2.25) (or, alternatively, invert the transforms (2.21)), which can be very hard in the general case. This solution is also expected to satisfy the exact Zwanzig equation (3.6), but it seems impossible even to check this.

(ii) The solution of the approximate Zwanzig equation (3.12), which is very likely to be very close to the exact one, but for the same reason solving (3.12) may prove to be as difficult as solving (2.25).

(iii) The solution (2.24) of the approximate convolutionless equation (2.23), which is not as close to the exact solution as the Zwanzig approximation, but the behaviour of which can be predicted much easier than that of either exact or Zwanzig approximate solutions.

(iv) Any further approximations, like the Markov limit of the Zwanzig equation or the van Hove limit of any solution. These procedures are not to be recommended because, as we have clearly seen in § 5, their predictions may prove to be completely wrong.

These are conclusions which can be drawn from our investigations of the formalism of master equations applied to the Friedrichs model. We think they are quite general and can be extended to other areas investigated with master equations. The approximate convolutionless equation works reasonably well in different situations, and we believe it may prove very useful on many occasions. On the other hand, the very popular formalism of master equations with a convolution is usually associated with the Markov or van Hove limits, which may obscure some interesting features of the dynamics of the system under consideration. Therefore, bearing in mind the extreme complexity of the Zwanzig formalism without the Markovian approximation, we wish to recommend the use of convolutionless equations whenever the existence of relevant superoperators can be proved.

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