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Quantum Theory of Dissipative Processes: The Markov Approximation Revisited

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Adopting the standard mathematical framework for describing reduced dynamics, we derive two formal identities for the density operator of an open quantum system. Each of these is equivalent to the old Nakajima–Zwanzig equation. The first identity is local in time. It contains the inverse of the dynamical map which governs the evolution of the density operator. We indicate a time interval on which this inverse exists. The second identity constitutes a suitable starting point for going beyond the Markov approximation in a controlled way. On the basis of the Bloch equations we argue once more that in studying quantum dissipation one has to pay attention to the von Neumann conditions. In the Nakajima–Zwanzig equation we make the first Born approximation. The ensuing master equation possesses the correct weak-coupling limit. While proving this rather obvious but at the same time important statement, we elucidate the mathematical methods which underlie the weak-coupling limit. Moving to a two-dimensional Hilbert space, we find that both for short and for long times our approximate master equation respects the von Neumann conditions. Assuming exponential decay for correlation functions, we propose a physical limit in which the solutions for the density operator become Markovian in character. We confirm the well-known statement that, as seen from a macroscopic standpoint, the system starts from an effective initial condition. The approach to equilibrium is exponential. The accessory relaxation constants can differ from the usual Bloch parameters $\gamma_\perp$ and $\gamma_\parallel$ by more than 50%.

KEY WORDS: Quantum dissipation; Markov approximation; von Neumann conditions; Bloch equations.

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1. INTRODUCTION

It is a well-known fact that the dynamical behavior of an open quantum system cannot be described by means of a wave function. In order to store all information on the system at a given time t, one needs to introduce a density operator $\rho(t)$.[1-3] Often, it is assumed that the evolution of the density operator is governed by a Markovian master equation $\dot{\rho}(t) = L\rho(t)$. The generator L is independent of time, and can be constructed such that the von Neumann conditions are fulfilled.[4] On the other hand, the time t may not be chosen negative. Hence, the Markov approximation has the drawback that irreversibility is brought in from the very outset.

Strictly speaking, the evolution of any open quantum system is completely reversible in time.[5] Under normal conditions, Poincaré recurrence times are very long, so that the evolution may be looked upon as an irreversible process. Sometimes, it is possible to really observe the reversible character of the dynamics. For instance, periodic energy exchange can occur between an atom and a finite number of electromagnetical modes.[6] It is obvious that in exploring such dynamics one cannot resort to the Markov approximation. Incidentally, the last remark may also apply to cases in which we do observe an irreversible evolution. As an illustration, we mention that for long times the decay of excited states can obey a power law.[7] The decay that is predicted on the basis of a Markovian master equation always takes place via exponential functions.[8,9]

The Markov approximation can be circumvented by proposing dynamical maps for the density operator the form of which differs from $\exp(Lt)$.[10-12] Unfortunately, these maps do not provide us with a useful master equation, because of ordering problems. Remember that a generic operator $O(t)$ does not commute with its time derivative. All in all, explicit evaluation of the density operator becomes a hard job.

In the present article we aim at improving on the Markov approximation by deriving a master equation right from the start. In the process of doing this, one must bear in mind three points. (i) Our equation should not have a phenomenological character. In other words, a definite relation should exist with the exact master equation for the density operator. (ii) The von Neumann conditions should be satisfied, i.e., the basic laws of quantum mechanics should be respected. (iii) In the Markovian limit the solution of our equation should coincide with the exact density operator. Although non-Markovian master equations[3] were already investigated during the 1960s,[13] the second point has received little attention up to

[3] As will be demonstrated later on, the exact master equation for the density operator can be cast in a form that is local in time. Hence, one should refrain from using the term "non-Markovian."[32] However, we shall adapt ourselves to the literature.

now. This is strange, because the von Neumann conditions impose restrictions on the rate at which relaxation takes place.[4] In Section 2 we discuss this issue at an elementary level.

One may severely doubt whether the above constraints allow for non-Markovian master equations that can be treated analytically. In Section 3 we derive an evolution equation which meets all constraints, except for the positivity of the density operator. The corresponding error can be made arbitrarily small at the expense of losing analytical simplicity. In the literature[11] it has been argued that such an approach can lead to physically relevant results. It should be remarked, however, that we shall confine ourselves to systems for which an external driving field is lacking.

Use will be made of the standard[14] mathematical framework for handling open quantum systems. This permits us to make a small excursion in Section 3. It has been conjectured[15] that the exact dynamical map for the density operator can be inverted. We construct the inverse, and specify a time interval on which it exists.

The simplest form of our non-Markovian master equation can be found in a straightforward way. In the exact evolution equation one has to discard all correlation functions of order three and higher, as well as all products of correlation functions.[13,16] For the ensuing equation we present in Section 4 a detailed discussion of constraints (ii) and (iii). Since our findings turn out to be quite reasonable, it makes sense to investigate under which circumstances the simplest non-Markovian master equation has solutions that possess a Markovian nature. This is the subject of Section 5.

In order to arrive at explicit results, the two-point correlation functions will be fitted to simple expressions that decay exponentially. For a two-level system we find that the time interval $[0, T]$, during which non-Markovian effects play a role, may be very short. It seems as if the system starts from an effective initial state, and subsequently evolves in a Markovian fashion. Besides effective initial conditions,[10] we also find effective values for relaxation constants. As shown in Section 6, differences from the usual constants $\gamma_{\perp}$ and $\gamma_{\parallel}$ can be surprisingly big.

This paper might appeal to a wide audience, because we do not work within the context of a specific model. For that reason our paper is self-contained, especially in discussing constraint (iii). The reference list contains a considerable number of textbooks. This should enable the interested reader to place the subject of quantum dissipation in a broader perspective. In the next section we briefly review the theory of Markovian master equations so as to develop a few ideas, and introduce some definitions.

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2. MARKOVIAN MASTER EQUATIONS

Consider a closed nonrelativistic quantum system. It is described by the density operator $\rho(t)$ which acts on the Hilbert space $\mathscr{H}$. If the Hamiltonian H' does not depend on the time t, then the density operator evolves according to $\rho(t) = \exp(-iHt)\,\rho(0)\exp(iHt)$, where the convention $H = H'/\hbar$ has been used. The expectation value $\langle H \rangle = \mathrm{Tr}(H\rho)$ is independent of time, so dissipation of energy cannot take place. It is well known[1-3] that the density operator fulfils the von Neumann conditions. These are given by

$$\mathrm{Tr}\,\rho(t) = 1, \qquad \rho^\dagger(t) = \rho(t), \qquad \langle \phi|\,\rho(t)\,|\phi\rangle \geqslant 0 \quad \forall\,|\phi\rangle \in \mathscr{H} \tag{1}$$

A fundamental way to introduce dissipation consists of coupling the quantum system $\mathscr{S}$ to a reservoir $\mathscr{R}$. One then departs from the following Hamiltonian:

$$H = H_{\mathscr{S}} \otimes 1_{\mathscr{R}} + 1_{\mathscr{S}} \otimes H_{\mathscr{R}} + \lambda V_{\mathscr{S}\mathscr{R}} \tag{2}$$

The coupling parameter λ lies in the interval $[0, 1]$. The operators $\rho(t)$ and H now act on the product Hilbert space $\mathscr{H}_{\mathscr{S}} \otimes \mathscr{H}_{\mathscr{R}}$. The Hilbert space $\mathscr{H}_{\mathscr{S}}$ may be of finite dimension. Although not beyond discussion,[10,17] it is customary to use the factorization $\rho(0) = \rho_{\mathscr{S}} \otimes \rho_{\mathscr{R}}$ as initial condition. Of course, both $\rho_{\mathscr{S}}$ and $\rho_{\mathscr{R}}$ must satisfy (1).

The expectation value of each system observable $O_{\mathscr{S}}$ can be written as $\mathrm{Tr}_{\mathscr{S}}[O_{\mathscr{S}}\rho_{\mathscr{S}}(t)]$. Hence, the reduced density operator $\rho_{\mathscr{S}}(t)$ is a quantity of central interest. Its time evolution is determined by[9]

$$\rho_{\mathscr{S}}(t) = \sum_{k,l=1}^{\infty} W_{kl}(t)\,\rho_{\mathscr{S}}\,W_{kl}^\dagger(t), \qquad \sum_{k,l=1}^{\infty} W_{kl}^\dagger(t)\,W_{kl}(t) = 1_{\mathscr{S}} \tag{3}$$

The operators $\{W_{kl}\}$ are defined as

$$\langle \phi|\,W_{kl}(t)\,|\chi\rangle = \lambda_l^{1/2}\langle \phi \otimes f_k|\,e^{-iHt}\,|\chi \otimes f_l\rangle \tag{4}$$

with $|\phi\rangle$ and $|\chi\rangle$ arbitrary states of $\mathscr{H}_{\mathscr{S}}$. Use has been made of the expansion $\rho_{\mathscr{R}} = \sum_{k=1}^{\infty} \lambda_k\,|f_k\rangle\langle f_k|$, where the reals $\{\lambda_k\}$ are nonnegative and satisfy the condition $\sum_{k=1}^{\infty} \lambda_k = 1$. The states $\{|f_k\rangle\}$ form an orthonormal basis of $\mathscr{H}_{\mathscr{R}}$. From (3) we infer that $\rho_{\mathscr{S}}(t)$ obeys the von Neumann conditions at all times.

In general, it is impossible to calculate the reduced density operator exactly. Often, a way out is offered by the Markov approximation. One adopts the following master equation as a starting point:

$$\dot{\rho}_{\mathscr{S}}(t) = L\rho_{\mathscr{S}}(t) \tag{5}$$

The generator L is a fixed linear operator that acts on the set of system density operators. The formal solution of (5) reads $\rho_{\mathscr{S}}(t) = \exp(Lt)\rho_{\mathscr{S}} \equiv \Lambda_t \rho_{\mathscr{S}}$. The map Λ_t has the semigroup property $\Lambda_{t+s} = \Lambda_t \Lambda_s$.

The Markovian master equation (5) can be constructed such that the von Neumann conditions are respected. One transforms (3)–(4) to the interaction picture, and takes the weak-coupling or van Hove[18] limit $t \to \infty$, $\lambda^2 = \tau/t$, with τ constant.[19] As an alternative, one may try to find all maps of the form (3) which possess the semigroup property.[4,20,21] This can be done by employing the mathematical notion of complete positivity.

The second method provides us with the most general Markovian master equation which does not violate the von Neumann conditions. By making a special choice of parameters one recovers the master equation that is obtained via the first method. The most general form of (5) can also be found by taking in (3)–(4) the singular-coupling limit.[22] However, the conditions under which this limit may be taken are rather unphysical.

Observe that the master equation (5) cannot be derived for both positive and negative times. Consider the weak-coupling limit, for instance, where the inequality $\tau \geqslant 0$ is manifest. Hence, if one invokes the Markov approximation, then the dynamical behavior of the system $\mathscr{S}$ will always be irreversible. Notice that the evolution described by (3) is completely reversible.[5]

While working with Markovian master equations it is important to be aware of the existence of the von Neumann conditions. To illustrate this remark, we set the dimension of $\mathscr{H}_{\mathscr{S}}$ equal to 2, and call the corresponding orthonormal basis $\{|1\rangle, |2\rangle\}$. Then an example of (5) is given by the famous[3,23–26] Bloch equations for the reduced density matrix $\rho_{ij} \equiv \langle i| \rho_{\mathscr{S}} |j\rangle$, with $i, j \in \{1, 2\}$. They read

$$\dot{\rho}_{12} = -(\gamma_\perp + i\omega_0)\rho_{12}, \qquad \dot{d} = -\gamma_{||}(d - d_\infty) \tag{6}$$

We defined $d = (\rho_{22} - \rho_{11})/2$. The inversion d and the constants $\gamma_\perp$, $\gamma_{||}$, ω_0, d_∞ are real.

Because of the relations $\rho_{11} + \rho_{22} = 1$ and $\rho_{21} = \rho_{12}^*$, the density matrix is completely determined by the solutions of (6). These are given by $\rho_{12}(t) = \rho_{12}(0)\exp[-(\gamma_\perp + i\omega_0)t]$ and $d(t) = d_\infty + [d(0) - d_\infty]\exp(-\gamma_{||}t)$. The density matrix is Hermitian and its trace equals 1, so we only have to check positivity.

A Hermitian matrix A with trace 1 is positive iff the inequality $|a_{12}|^2 \leqslant a_{11}a_{22}$ is obeyed. For the reduced density matrix this inequality comes out as

$$|\rho_{12}(t)|^2 + d(t)^2 \leqslant \tfrac{1}{4} \tag{7}$$

Since $\rho_{\mathscr{S}}(0)$ is a density operator, the above condition is equivalent to the following set of constraints:

$$|d_\infty| \leqslant \tfrac{1}{2}; \qquad \gamma_\perp, \gamma_{||} \geqslant 0; \qquad \gamma_{||}/\gamma_\perp \leqslant 2 \tag{8}$$

The necessity of the last constraint follows by taking $\rho_{12}(0) = |d_\infty| = 1/2$, $d(0) = 0$, and $t \to \infty$. To prove sufficiency of (8) one should notice that $2\,|d(t)| \leqslant f(t) \equiv 1 - (1 - 2\,|d(0)|) \exp(-\gamma_{||} t)$. Furthermore, one has $[1 - 4d(0)^2] \exp(-\gamma_{||} t) \leqslant 1 - f(t)^2$. By combining these inequalities with (8) we can derive (7). Altogether, we see that the Bloch equations (6) respect the von Neumann conditions iff (8) is true.

Traditionally, the Bloch equations are derived[3,23] by writing down the perturbative series

$$e^{iH_0 t} \rho(t) e^{-iH_0 t} = \rho(0) + \sum_{n=1}^{\infty} (-\lambda)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n\, T^{(n)}(t_1, t_2, ..., t_n) \tag{9}$$

and discarding all contributions of order λ^3 and higher. The operators $\{T^{(n)}\}$ are defined as

$$T^{(n)}(t_1, t_2, ..., t_n) = i^n [V(t_1), [V(t_2), ..., [V(t_n), \rho(0)] ...]] \tag{10}$$

with $V(t) = \exp(iH_0 t)\, V_{\mathscr{S}\mathscr{R}} \exp(-iH_0 t)$ and $H_0 = H(\lambda = 0)$. The operator on the left-hand side of (9) has trace one, as well as the operator $\rho(0)$.

Since each operator $T^{(n)}$ has zero trace and is self-adjoint, the matrix element $\langle \Psi_n | T^{(n)} | \Psi_n \rangle$ is negative for certain states $|\Psi_n\rangle \in \mathscr{H}$. Therefore, by truncating the right-hand side of (9) the positivity of the left-hand side might be destroyed. This may lead to erroneous predictions. Indeed, if the Bloch equations are derived on the basis of fourth-order perturbation theory, then one finds[27] that $\gamma_{||}$ can be greater than $2\gamma_\perp$. In view of (8) such a prediction contradicts the von Neumann conditions.

3. ALTERNATIVES TO THE NAKAJIMA–ZWANZIG EQUATION

As appears from the previous section, there exists a well-developed theory on quantum dynamical maps which have the semigroup property. This theory can be utilized to make detailed predictions on the time evolution of system observables.[9,17,28] For the exact map (3)–(4) the situation is entirely different. One can merely prove formal results which are of little use as seen from a practical point of view. For instance, a formal identity for the reduced density operator can be derived, which is known as the Nakajima–Zwanzig equation.[17],[4]

Below we shall demonstrate that the Nakajima–Zwanzig equation is not the only exact result that can be established. There exist other formal identities for the reduced density operator. These might be of help in gaining further information on the map (3)–(4). We shall start at an abstract mathematical level, and work in the same setting as Davies.[14,19]

All density operators ρ acting on $\mathscr{H}$ are elements of a Banach space $\mathscr{B}$ with norm $\|\cdot\|_1$.[29] The subscript 1 will be omitted. We suppose that $\exp(Zt)$ and $\exp[(Z+\lambda A)t]$ are strongly continuous one-parameter groups of isometries on $\mathscr{B}$, with $\lambda \in [0, 1]$. The operator A has domain $\mathscr{B}$, and is bounded with respect to the sup-norm on $\mathscr{B}$. The operators P_0 and $P_1 \equiv 1 - P_0$ are projections on $\mathscr{B}$ which commute with the generator Z. We employ the abbreviations $\mathscr{B}_i = P_i\mathscr{B}$, $Z_i = P_i Z$, and $O_{ij} = P_i O P_j$, with O an operator on $\mathscr{B}$. In Section 4 we shall give a physical meaning to the operators A, P_0, and Z.

In the interaction picture the reduced density operator is formally given by

$$W_{00}(t)\rho = e^{-(Z_0+\lambda A_{00})t} P_0 \, e^{(Z+\lambda A)t} \, P_0 \rho \tag{11}$$

The operator $W_{00}(t)$ has domain $\mathscr{B}$; the operators $\exp[(Z_0 + \lambda A_{00})t]$ form a one-parameter group of isometries (ref. 14, pp. 138, 139). Let $\exp[(E+F)t]$ and $\exp(Et)$ be one-parameter groups on $\mathscr{B}$. If the operator F is bounded, then one can prove the identity (ref. 14, pp. 68, 69)

$$e^{(E+F)t}\rho = e^{Et}\rho + \int_0^t ds \, e^{E(t-s)} \, F e^{(E+F)s} \rho \tag{12}$$

where t is positive.

We replace the generator $E+F$ by $Z+\lambda A$. The choices $F=\lambda A_{01}$ and $F=\lambda A_{10}$ lead to the following Nakajima–Zwanzig equation (ref. 14, pp. 138, 139):

$$W_{00}(t)\rho = P_0\rho + \lambda^2 \int_0^t ds \int_0^s du \, \tilde{A}_{01}(s) \, \tilde{A}_{10}(u) \, W_{00}(u)\rho \tag{13}$$

with t positive. We defined

$$\tilde{A}_{ij}(t)\rho = e^{-(Z_i+\lambda A_{ii})t} \, A_{ij} \, e^{(Z_j+\lambda A_{jj})t} \rho \tag{14}$$

[4] Ref. 17 lists all of the original papers on the Nakajima–Zwanzig equation.

On each closed interval $[0, t_0]$ the operators $W_{00}(t)$ and $\tilde{A}_{ij}(t)$ are uniformly bounded by the real number $M \exp(\alpha t_0)$, where α and M are positive (ref. 14, pp. 68, 69). Together with (13) this implies the existence of a real function $m(t)$ and positive constants a, ε such that

$$\| W_{00}(t) P_0 \rho \| \geqslant m(t) \|P_0 \rho\| \qquad \forall \rho \in \mathscr{B} \tag{15}$$

where $m(t) > \varepsilon$ for $t \in [0, a]$. Hence, on the interval $[0, a]$ the operator $W_{00}(t)$ with domain $\mathscr{B}_0$ possesses a bounded inverse.[30] The norm $\| W_{00}^{-1}(t) \|$ is uniformly bounded by the constant $1/\varepsilon$. From this property and continuity of $W_{00}(t)\rho$ we deduce that the element $W_{00}^{-1}(t)\rho$ of $\mathscr{B}$ is continuous on the interval $[0, a]$ with respect to the norm on $\mathscr{B}$.

In order to construct the operator $W_{00}^{-1}(t)$, we replace in (13) t by s as well as ρ by $W_{00}^{-1}(t)\rho$. The ensuing equation contains the operators $W_{00}^{-1}(t)$ and $U_{00}(s, t) \equiv W_{00}(s)\, W_{00}^{-1}(t)$. The former can be eliminated by replacing in (13) ρ by $W_{00}^{-1}(t)\rho$ once more. We now arrive at

$$U_{00}(s, t)\rho = P_0 \rho - \lambda^2 \int_s^t du \int_0^u dv\, \tilde{A}_{01}(u)\, \tilde{A}_{10}(v)\, U_{00}(v, t)\rho \tag{16}$$

with $0 \leqslant s \leqslant t \leqslant a$.

All of the operators figuring in the integrand of (16) are uniformly bounded on the interval $[0, a]$. Therefore, the integral equation (16) can be solved formally by performing an iteration *ad infinitum*. One finds

$$\begin{aligned} U_{00}(s, t)\rho &\\ = P_0 \rho + \sum_{n=1}^{\infty} (-\lambda^2)^n \int_s^t dt_1 \int_0^{t_1} dt_2 \int_{t_2}^t dt_3 \int_0^{t_3} dt_4 \cdots \int_{t_{2n-2}}^t dt_{2n-1} \int_0^{t_{2n-1}} dt_{2n} &\\ \times \tilde{A}_{01}(t_1)\, \tilde{A}_{10}(t_2)\, \tilde{A}_{01}(t_3)\, \tilde{A}_{10}(t_4) \cdots \tilde{A}_{01}(t_{2n-1})\, \tilde{A}_{10}(t_{2n})\rho & \end{aligned} \tag{17}$$

We iterate (13) and act with the series for the operator $W_{00}(t)$ on the iterative solution for $U_{00}(s = 0, t)\rho$. The outcome is $P_0 \rho$, as expected.

Owing to the result (17), one can derive an identity which may be compared to the Markovian master equation (5). From (13) it is manifest that the time derivative of $W_{00}(t)\rho$ exists for all $\rho \in \mathscr{B}$. With the help of the operator $U_{00}(s, t)$ the derivative can be cast into the following form:

$$\frac{d}{dt} [W_{00}(t)\rho] = L_{00}(t)\, W_{00}(t)\rho \tag{18}$$

We made use of the definition

$$L_{00}(t)\rho = \lambda^2 \tilde{A}_{01}(t) \int_0^t ds\, \tilde{A}_{10}(s)\, U_{00}(s, t)\rho \tag{19}$$

with $0 \leqslant t \leqslant a$.

The formal master equation (18) and the Markov equation (5) have two properties in common: all of the time arguments are equal to each other, and for each operator the domain and the range lie inside the subspace $\mathscr{B}_0$. At the same time, the identity (18) is equivalent to the Nakajima–Zwanzig equation (13). The complicated operator $L_{00}(t)$ can be evaluated formally by employing (17). We remark that equations of the type (18) have been used to study quantum dissipation in the presence of external fields (ref. 31; ref. 9, p. 40). We should also mention that there exist several methods for making the exact evolution equation local in time.[15,16,32,33]

One may raise the question of whether the interval $[0, a]$ extends to physically interesting times. For $A_{11} = 0$ we can give an estimate of a by making use of the assumption (ref. 14, p. 143)

$$\int_0^\infty dx\, \|A_{01} e^{Z_1 x} A_{10}\| \equiv b < \infty \tag{20}$$

One can generate the above integral in (13) by interchanging the order of integration. It turns out that one may choose $m(t) = 2 - \exp(\lambda^2 bt)$ in (15), so that we find $(\log 2)/(\lambda^2 b)$ as an upper bound for a. Hence, for $A_{11} = 0$ the result (5) can be derived from (18) by taking the weak-coupling limit, provided that $\tau = \lambda^2 t$ is smaller than $(\log 2)/b$. The last statement remains true if we allow the operator A_{11} to differ from zero. This can be proved on the basis of assumption (5.13) of ref. 14.

We come to the discussion of a second identity for the reduced density operator. Choose $E = Z$ and $F = \lambda A$ in (12), and iterate the ensuing integral equation n times. Put projectors P_0 around each term so that an equation for the operator $P_0 \exp[(Z + \lambda A)t]\, P_0$ is created. It contains an n-fold integral with the operator $(P_0 + P_1) \exp[(Z + \lambda A)t]\, P_0$ under the last integral sign. Elaborate this operator by using the identity (12) twice. The choices to be made are $E + F = Z + \lambda A$, $F = \lambda A_{10}$ and $E = Z_1$, $F = \lambda A_{11}$.

Going over to the interaction picture and taking the operator A_{00} equal to zero, we finally arrive at the identity

$$\begin{aligned} W_{00}(t)\rho = P_0\rho &+ \sum_{k=1}^{n-1} \lambda^k \int_0^t dt_1 \cdots \int_0^{t_{k-1}} dt_k\, C_{00}^{(k)}(t_1, \ldots, t_k)\rho \\ &+ \lambda^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n\, C_{00}^{(n)}(t_1, \ldots, t_n)\, W_{00}(t_n)\rho \end{aligned}$$

$$+\lambda^{n+1}\int_0^t dt_1\cdots\int_0^{t_n} dt_{n+1}\, C_{00}^{(n+1)}(t_1,\ldots, t_{n+1})\, W_{00}(t_{n+1})\rho$$

$$+\lambda^{n+2}\int_0^t dt_1\cdots\int_0^{t_{n+1}} dt_{n+2}\, C_{01}^{(n)}(t_1,\ldots, t_n)$$

$$\times e^{-Zt_{n+1}}A_{11}e^{(Z_1+\lambda A_{11})(t_{n+1}-t_{n+2})}A_{10}e^{Zt_{n+2}}\,W_{00}(t_{n+2})\rho \qquad (21)$$

with t positive and n a positive integer. We used the abbreviations

$$C_{ij}^{(n)}(t_1,\ldots, t_n)\rho = P_i A(t_1)\, A(t_2)\cdots A(t_n)\, P_j\rho \qquad (22)$$

and $A(t) = \exp(-Zt)A\exp(Zt)$.

If A_{00} equals zero, then (21) is an exact equation for the reduced density operator. In deriving such equations one has to use one-parameter groups the generator of which depends on the awkward projector P_1. The advantage of (21) is that all of the troublesome operators have been gathered in one single contribution, which vanishes if A_{11} equals zero.

Let us discard in (21) the term containing A_{11}, and replace $W_{00}(t)$ by the new operator $W_{00}(t; n)$. The ensuing equation is of practical value, because one-parameter groups other than $\exp(Zt)$ no longer occur. The latter describes the free evolution of the system and reservoir. We have to admit, however, that the operator $W_{00}(t; n)\rho$ does not automatically obey the von Neumann conditions. To be specific, the operator $W_{00}(t; n)\rho$ is self-adjoint and has trace 1, but its positivity is not guaranteed.

The right-hand side of (21) includes the first n terms out of the perturbation expansion for $W_{00}(t)\rho$. Therefore, the difference between the operators $W_{00}(t)\rho$ and $W_{00}(t; n)\rho$ is of the order λ^n at least. In other words, a time interval $[0, t_0]$ will exist on which the operators $W_{00}(t)\rho$ and $W_{00}(t; n)\rho$ almost coincide. As long as $0 \leqslant t \leqslant t_0$ the condition of positivity cannot be severely violated. Note that the greater we choose the integer n, the greater the time t_0 will be. One can rigorously prove that for all $\rho \in \mathscr{B}$ and $a > 0$ the operator $W_{00}(t; n)\rho$ converges to $W_{00}(t)\rho$ uniformly on $[0, a]$ as $n \to \infty$.

If A_{11} equals zero, the operators $W_{00}(t)\rho$ and $W_{00}(t; n)\rho$ do not differ from each other. In the weak-coupling limit the operator A_{11} does not figure in the master equation for the reduced density operator.[19] Hence, one expects that also for large times and small coupling parameter the condition of positivity does not cause any difficulties.

The identity (21) is a useful alternative to the Nakajima–Zwanzig equation. It gives us the opportunity to approximate the reduced density operator in a controlled way, and respect the von Neumann conditions to some extent.

4. NON-MARKOVIAN MASTER EQUATION FOR AN N-LEVEL SYSTEM

Leaving the abstract mathematical level, we apply the ideas of the last section to the physical problem of quantum dissipation. To that end, we must define

$$\begin{aligned} Z\rho &= -i[H_{\mathscr{S}}\otimes 1_{\mathscr{R}} + 1_{\mathscr{S}}\otimes H_{\mathscr{R}}, \rho] \\ A\rho &= -i[V_{\mathscr{S}\mathscr{R}}, \rho] \\ P_0\rho &= (\mathrm{Tr}_{\mathscr{R}}\,\rho)\otimes\rho_{\mathscr{R}} \end{aligned} \tag{23}$$

The operators on the right-hand side have been introduced in Section 2. We assume that the operators $\rho_{\mathscr{R}}$ and $H_{\mathscr{R}}$ commute. Then the projector P_0 commutes with the generator Z, as supposed in the previous section.

We factorize the interaction potential as follows:

$$V_{\mathscr{S}\mathscr{R}} = \sum_{\alpha} V_\alpha \otimes U_\alpha \tag{24}$$

The operators V_α and U_α act on $\mathscr{H}_{\mathscr{S}}$ and $\mathscr{H}_{\mathscr{R}}$, respectively. By modifying the Hamiltonian $H_{\mathscr{S}}$ we can shift each potential U_α such that $\mathrm{Tr}_{\mathscr{R}}(U_\alpha\rho_{\mathscr{R}})$ equals zero. This implies that A_{00} can be put equal to zero without loss of generality. As anticipated in Section 3, the operator A_{11} never equals zero if definitions (23) are employed.

In the following we shall work with a Hilbert space $\mathscr{H}_{\mathscr{S}}$ of finite dimension N. The Hamiltonian $H_{\mathscr{S}}$ has nondegenerate eigenvalues $\{\varepsilon_k\}_{k=1}^N$, with $\{|k\rangle\}_{k=1}^N$ being the set of accessory eigenvectors. Given these assumptions, our quantum system $\mathscr{S}$ is described by the density matrix $\rho_{kl}(t) \equiv \langle k|\,\rho_{\mathscr{S}}(t)\,|l\rangle$. We may identify $\mathscr{B}_0$ with the Banach space $\mathscr{M}(N)$ of complex $(N\times N)$ matrices. The norm of matrix M is given by $\|M\| = \sup\{\|Mx\|/\|x\|\colon x\in \mathbb{C}^N,\ x\neq 0\}$.

Remember that the matrix $\rho\in\mathscr{M}$ is a density matrix iff ρ is Hermitian and has positive eigenvalues, the sum of which equals 1. The norm of the density matrix ρ is equal to its largest eigenvalue. One can easily prove the following important statement[34]: if a sequence $\{\rho_n\}$ of density matrices converges to an element ρ of $\mathscr{M}$ with respect to the norm on $\mathscr{M}$, then ρ is a density matrix. Furthermore, $\mathrm{Tr}(\rho_n M)$ converges to $\mathrm{Tr}(\rho M)$ for all $M\in\mathscr{M}$.

In the interaction picture the reduced density operator $\rho_{\mathscr{S}}(t)$ is given by $\mathrm{Tr}_{\mathscr{R}}[W_{00}(t)\,\rho(0)]$. Following the earlier discussion we replace $W_{00}(t)$ by the operator $W_{00}(t;n)$. We set integer n equal to 1. Then the presence of the reservoir manifests itself via two-point correlation functions. These are defined by

$$c_{\alpha\beta}(t) = \mathrm{Tr}_{\mathscr{R}}(e^{iH_{\mathscr{R}}t} U_\alpha e^{-iH_{\mathscr{R}}t} U_\beta \rho_{\mathscr{R}}) \tag{25}$$

Upon using the relations (21)–(25), we obtain the following master equation:

$$\rho^{(1)}_{\mathscr{S}}(t) = \rho_{\mathscr{S}} + \lambda^2 \int_0^t ds\, L(t-s, s)\, \rho^{(1)}_{\mathscr{S}}(s) \tag{26}$$

with t positive. The superscript (1) reminds us of the replacement $W_{00}(t) \to W_{00}(t; n=1)$. The operator L stands for the sum $\sum_{j=1}^4 L_j$, where the linear operators $\{L_j\}$ act on $\mathscr{M}$. They are defined by

$$\begin{aligned} L_1(t,s)\rho &= \int_0^t du \sum_{\alpha\beta} c_{\alpha\beta}(u)\ V_\beta(s)\, \rho V_\alpha(s+u) \\ L_2(t,s)\rho &= -\int_0^t du \sum_{\alpha\beta} c_{\alpha\beta}(u)\ V_\alpha(s+u)\ V_\beta(s)\rho \end{aligned} \tag{27}$$

and $L_{j+2}(t,s)\rho = [L_j(t,s)\rho^\dagger]^\dagger$, with $j=1,2$. The matrix $V_\alpha(t) \in \mathscr{M}$ is equal to $\exp(iH_{\mathscr{S}}t)\ V_\alpha \exp(-iH_{\mathscr{S}}t)$. Use has been made of the symmetry relation $c^*_{\beta\alpha}(-t) = c_{\alpha\beta}(t)$. We should mention that (26)–(27) can be directly obtained from the Nakajima–Zwanzig equation (13) by putting the operators A_{00} and A_{11} equal to zero.

The fact that $L_j\rho$ exists for all $\rho \in \mathscr{M}$ implies that the operator L_j is bounded, because $\mathscr{M}$ is of finite dimension. Since $\exp(iH_{\mathscr{S}}t)$ is a unitary matrix, the norm $\|V_\alpha(t)\|$ does not depend on time. From (26)–(27) it is manifest that the norm $\|\rho^{(1)}_{\mathscr{S}}(t)\|$ is a continuous function of time. It therefore is uniformly bounded on each closed time interval. The same holds true for the norm $\|L(t,s)\rho\|$, and thus, by the fact that $\mathscr{M}$ is of finite dimension, for the norm $\|L(t,s)\|$. Hence, it is permitted to represent the matrix $\rho^{(1)}_{\mathscr{S}}(t)$ by iterating (26) *ad infinitum.*

In Section 3 we have argued that in the weak-coupling limit the elements $\rho_{\mathscr{S}}(t)$ and $\rho^{(1)}_{\mathscr{S}}(t)$ of $\mathscr{M}$ converge to the same density matrix. We prove this statement by discussing the weak-coupling limit of (26). We shall find some useful results which will be needed later on.

The following two assumptions are standard[4,9,19,35]:

$$\sum_\alpha \|V_\alpha\| \equiv v < \infty, \qquad \sup_{\alpha\beta} \int_0^\infty dt\ |c_{\alpha\beta}(t)| \equiv c < \infty \tag{28}$$

If (28) is true, then the matrix $\rho^{(1)}_{\mathscr{S}}(t/\lambda^2)$ converges to $\sigma(t) \in \mathscr{M}$ uniformly on each closed interval $[0, a]$ as $\lambda \to 0$. The density matrix $\sigma(t)$ satisfies the Markovian equation $\dot{\sigma}(t) = L_0 \sigma(t)$, with $\sigma(0) = \rho_{\mathscr{S}}$. In the basis $\{|k\rangle\}$ the operator L_0 with domain $\mathscr{M}$ is determined by

$$(L_0\rho)_{kl} = \sum_{\alpha\beta mn} \delta(\omega_{km} + \omega_{nl}, 0)\, \tilde{c}_{\alpha\beta}(\omega_{nk})\, V_{\alpha,nl} V_{\beta,km} \rho_{mn}$$

$$- \sum_{\alpha\beta m} i\hat{c}_{\alpha\beta}(\omega_{km})\, V_{\alpha,km} V_{\beta,mk} \rho_{kl} + \sum_{\alpha\beta m} i\hat{c}^*_{\alpha\beta}(\omega_{lm})\, V_{\alpha,ml} V_{\beta,lm}\, \rho_{kl} \tag{29}$$

where $\delta(a, b)$ denotes a Kronecker delta, and ω_{kl} stands for the difference $\varepsilon_k - \varepsilon_l$. The following two transforms have been used:

$$\tilde{f}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t} f(t), \qquad i\hat{f}(z) = \int_0^{\infty} dt\, e^{izt} f(t) \tag{30}$$

By the symbol $\hat{f}^*$ the complex conjugate of the transform $\hat{f}$ is meant. We defer the proof of (29) to Appendix A. The weak-coupling limit of the exact equation (13) requires more input than (28). As discussed in the literature,[4,9,19,35] it also leads to the above master equation for the density matrix $\sigma(t)$.

For $N = 2$ the density matrix $\sigma(t)$ obeys the Bloch equations.[5] The Bloch parameters are given by

$$\gamma_{\parallel} = \sum_{\alpha\beta} [\tilde{c}_{\alpha\beta}(\omega_{12}) + \tilde{c}_{\beta\alpha}(\omega_{21})]\, V_{\alpha,12} V_{\beta,21}, \qquad \gamma_{\perp} = \gamma_{\parallel}(\tfrac{1}{2} + \Gamma)$$

$$\gamma_{\parallel}\Gamma = \tfrac{1}{2} \sum_{\alpha\beta} \tilde{c}_{\alpha\beta}(0)(V_{\alpha,11} - V_{\alpha,22})(V_{\beta,11} - V_{\beta,22})$$

$$\gamma_{\parallel} d_{\infty} = \tfrac{1}{2} \sum_{\alpha\beta} [\tilde{c}_{\alpha\beta}(\omega_{12}) - \tilde{c}_{\beta\alpha}(\omega_{21})]\, V_{\alpha,12} V_{\beta,21}$$

$$\omega_0 = \mathrm{Re} \sum_{\alpha\beta} [\hat{c}_{\alpha\beta}(\omega_{12}) - \hat{c}^*_{\alpha\beta}(\omega_{21})]\, V_{\alpha,12} V_{\beta,21}$$

$$+ \mathrm{Re} \sum_{\alpha\beta} \hat{c}_{\alpha\beta}(0)(V_{\alpha,11} - V_{\alpha,22})(V_{\beta,11} + V_{\beta,22}) \tag{31}$$

[5] At this point we would like to make a small comment. For a two-level system the weak-coupling limit as discussed by Davies[19] generates the standard[3,23–26] Bloch equations (6). Hence, the results of Davies should not be characterized as "physically unacceptable"; cf. ref. 36.

At this point Bochner's theorem comes in.[37] Let $f(t)$ be a complex-valued, bounded, and continuous function on R, with the property

$$\sum_{k,l=1}^{n} y_k y_l^* f(t_k - t_l) \geqslant 0 \qquad \forall n \geqslant 1 \tag{32}$$

where $\{t_k\} \subset \mathrm{R}$ and $\{y_k\} \subset \mathrm{C}$ are arbitrary sets. Then for all $\omega \in \mathrm{R}$ the Fourier transform $\hat{f}(\omega)$ as defined under (30) is real and nonnegative. The above constraints are obeyed by any function $f(t) = \sum_{\alpha\beta} c_{\alpha\beta}(t)\, v_\alpha v_\beta^*$, with $\{v_\alpha\}$ a subset of C. Consequently, relations (31) are in accordance with rules (8). This was to be expected because $\sigma(t)$ is a density matrix.

Next, we examine the master equation (26) for small times and the case $N = 2$. Then the Hermitian matrix ρ is a density matrix iff the constraints $\mathrm{Tr}\,\rho = 1$ and $\mathrm{Tr}\,\rho^2 \leqslant 1$ are satisfied. From (26) it is obvious that the matrix $\rho_{\mathscr{S}}^{(1)}(t)$ is Hermitian, and that the trace equals 1. Inspired by the observations made in Section 3, we shall prove the existence of a time interval $[0, t_0]$ on which the inequality $\mathrm{Tr}\,\rho_{\mathscr{S}}^{(1)}(t)^2 \leqslant 1$ is true.

If $\mathrm{Tr}\,\rho_{\mathscr{S}}(0)^2 < 1$, then the time interval surely exists, so we may assume that the system starts from a pure state. The function $\mathrm{Tr}\,\rho_{\mathscr{S}}^{(1)}(t)^2$ possesses both a first-order and a second-order time derivative. From (26)–(27) one infers that at $t = 0$ the former equals zero, whereas the latter is given by

$$4\lambda^2 \sum_{\alpha\beta klmn} c_{\alpha\beta}(0)\, \rho_{kl}(0) [\rho_{mn}(0)\, V_{\alpha,nk} V_{\beta,lm} - \rho_{lm}(0)\, V_{\alpha,mn} V_{\beta,nk}] \tag{33}$$

Note that at $t = 0$ the superscript of $\rho_{\mathscr{S}}^{(1)}(t)$ may be omitted.

After substitution of $\rho_{12}(0) = [\rho_{11}(0)\, \rho_{22}(0)]^{1/2} \exp(i\theta)$ and use of definition (25), the derivative takes the following form:

$$\left.\frac{d^2}{dt^2} \mathrm{Tr}\,\rho_{\mathscr{S}}^{(1)}(t)^2 \right|_{t=0} = -4\lambda^2\, \mathrm{Tr}_{\mathscr{R}}(W^\dagger W \rho_{\mathscr{R}}) \tag{34}$$

with the operator W defined as

$$\begin{aligned} W = \sum_\alpha U_\alpha \{ & [\rho_{11}(0)\, \rho_{22}(0)]^{1/2} (V_{\alpha,11} - V_{\alpha,22}) \\ & - \rho_{11}(0)\, V_{\alpha,21} e^{i\theta} + \rho_{22}(0)\, V_{\alpha,12} e^{-i\theta} \} \end{aligned} \tag{35}$$

The derivative is negative, so by the continuity of $\rho_{\mathscr{S}}^{(1)}(t)$ the interval $[0, t_0]$ indeed exists. Observe that at $t = 0$ the second-order time derivatives of $\rho_{\mathscr{S}}^{(1)}(t)$ and $\rho_{\mathscr{S}}(t)$ are equal to each other.

The above conclusion is nontrivial as becomes clear from the following example: choose in the Bloch equations $d_\infty = -1/2$ and $2\gamma_\perp = \gamma_\parallel - \delta$, with δ positive. Because of (8) this choice of parameters leads to contradictions with the von Neumann condition (7). The problems already occur for arbitrarily small times. Start from the pure state given by $\rho_{12} = \rho_{21} = (\rho_{11}\rho_{22})^{1/2}$ and $\rho_{11} = 1 - \rho_{22} = [1 + \delta/(2\gamma_\parallel)]^{-1}$. Then there does not exist a finite time interval $[0, t_0]$ on which (7) is true.[38]

Choosing $N = 2$, we write down the master equation (26) in the basis $\{|1\rangle, |2\rangle\}$. For notational reasons we suppress all of the superscripts (1). Introducing again the inversion $d(t) = [\rho_{22}(t) - \rho_{11}(t)]/2$, and returning to the Schrödinger picture, we arrive at the following set of equations:

$$
\begin{aligned}
\rho_{12}(t) &= e^{-i\omega t}\rho_{12}(0) + \lambda^2 \int_0^t ds\, (e^{-i\omega t} - e^{-i\omega s})\, h(s) \\
&\quad - \lambda^2 \int_0^t ds \int_0^{t-s} du\, e^{-i\omega(t-s)}[f_1(u)\,\rho_{12}(s) - f_2(u)\,\rho_{21}(s) - f_3(u)\, d(s)] \\
d(t) &= d(0) + \lambda^2 \int_0^t ds\, (t-s)\, g(s) \\
&\quad + \lambda^2 \int_0^t ds \int_0^{t-s} du\, [f_4(u)\,\rho_{12}(s) + f_4^*(u)\,\rho_{21}(s) - f_5(u)\, d(s)]
\end{aligned} \tag{36}
$$

with $\omega \equiv \omega_{12}$. The new functions are defined as follows:

$$
\begin{aligned}
f_1(t) &= \sum_{\alpha\beta} [c'_{\alpha\beta}(t)\, S_{\alpha,-} S_{\beta,-} - ic''_{\alpha\beta}(t)\, S_{\alpha,-} S_{\beta,+} + 2c'_{\alpha\beta}(t)\, e^{i\omega t}\, V_{\alpha,12} V_{\beta,21}] \\
f_2(t) &= 2e^{i\omega t} \sum_{\alpha\beta} c'_{\alpha\beta}(t)\, V_{\alpha,12} V_{\beta,12} \\
f_3(t) &= 2 \sum_{\alpha\beta} [c'_{\alpha\beta}(t)\, S_{\alpha,-} V_{\beta,12} - ic''_{\alpha\beta}(t)\, e^{i\omega t} V_{\alpha,12} S_{\beta,+}] \\
f_4(t) &= e^{-i\omega t} \sum_{\alpha\beta} [c'_{\alpha\beta}(t)\, V_{\alpha,21} S_{\beta,-} - ic''_{\alpha\beta}(t)\, V_{\alpha,21} S_{\beta,+}] \\
f_5(t) &= 2 \sum_{\alpha\beta} c'_{\alpha\beta}(t)[e^{i\omega t} V_{\alpha,12} V_{\beta,21} + e^{-i\omega t} V_{\alpha,21} V_{\beta,12}] \\
g(t) &= i \sum_{\alpha\beta} c''_{\alpha\beta}(t)[e^{i\omega t} V_{\alpha,12} V_{\beta,21} - e^{-i\omega t} V_{\alpha,21} V_{\beta,12}] \\
h(t) &= \omega^{-1} \sum_{\alpha\beta} c''_{\alpha\beta}(t)[e^{i\omega t} V_{\alpha,12} S_{\beta,-} - S_{\alpha,-} V_{\beta,12}]
\end{aligned} \tag{37}
$$

with $z' \equiv \mathrm{Re}\, z$, $z'' \equiv \mathrm{Im}\, z$ for all $z \in \mathrm{C}$, and $S_{\alpha,\pm} \equiv V_{\alpha,22} \pm V_{\alpha,11}$.

We investigate the asymptotic behavior of (36) for the case that the coupling parameter λ has a fixed value. Suppose that there are constants $\bar{\rho}_{12}$ and $\bar{d}$ such that the functions $\rho_{12}(t)\exp(i\omega t)-\bar{\rho}_{12}$, $d(t)-\bar{d}$, and $\sup_{\alpha\beta}|tc_{\alpha\beta}(t)|$ converge to zero as t becomes large. Divide the two equations (36) by t, and let t go to infinity. Employ assumptions (28) and the fact that $\lim_{t\to\infty} t^{-1}\int_0^t ds\,|f(s)|=0$ for any continuous function $f(t)$ that vanishes as t becomes large. We end up with the result

$$\bar{\rho}_{12}=0, \qquad \bar{d}\doteq\int_0^\infty dt\,g(t)\bigg/\int_0^\infty dt\,f_5(t)=d_\infty \tag{38}$$

The last equality follows from (31) and (37).

In short, if the solutions $\rho_{12}(t)$ and $d(t)$ of (36) converge for fixed λ and t going to infinity, then their limiting values are equal to zero and d_∞, respectively. These are the values of the weak-coupling limit. Hence, for almost all initial conditions the master equation (36) will obey the von Neumann condition (7), with t sufficiently large and λ finite.

5. EXPONENTIAL FIT FOR THE CORRELATION FUNCTION OF THE RESERVOIR

In the remainder of this paper we shall study the evolution equations (36). They can be reduced to a set of algebraic equations by means of Laplace transformation. One finds

$$\begin{pmatrix} z-\omega-\lambda^2\hat{f}_1(z-\omega) & \lambda^2\hat{f}_2(z-\omega) & \lambda^2\hat{f}_3(z-\omega) \\ -\lambda^2\hat{f}_2^*(-z^*-\omega) & z+\omega+\lambda^2\hat{f}_1^*(-z^*-\omega) & -\lambda^2\hat{f}_3^*(-z^*-\omega) \\ \lambda^2\hat{f}_4(z) & -\lambda^2\hat{f}_4^*(-z^*) & z-\lambda^2\hat{f}_5(z) \end{pmatrix}\begin{pmatrix}\hat{\rho}_{12}(z)\\ \hat{\rho}_{21}(z)\\ \hat{d}(z)\end{pmatrix}$$
$$=\begin{pmatrix}\rho_{12}(0)+i\omega\lambda^2\hat{h}(z-\omega)/z\\ \rho_{21}(0)+i\omega\lambda^2\hat{h}^*(-z^*-\omega)/z\\ d(0)-\lambda^2\hat{g}(z)/z\end{pmatrix} \tag{39}$$

The transform $\hat{f}$ was defined under (30). Again, by $\hat{f}^*(z)$ the complex conjugate of the transform $\hat{f}(z)$ is meant. Application of Cramers' rule and use of the inverse transformation $f(t)=i(2\pi)^{-1}\int_C dz\exp(-izt)\hat{f}(z)$ gives us the solutions of (36); contour C is defined by the prescription z'' is constant and positive. Unfortunately, we meet integrals that cannot be evaluated easily. They contain the Laplace transform of the reservoir correlation function.

In order to simplify (39) we first replace the potentials $\{U_\alpha\}$ by a single potential U, so that one may write $c_{\alpha\beta}(t)=c(t)$. As a consequence, we encounter the sums $\sum_\alpha S_{\alpha,\pm}$ in (37). These are assumed to be equal to zero. Consider for instance a two-level atom which interacts with the radiation field via its electric dipole. If the states $\{|1\rangle, |2\rangle\}$ have a definite parity, then the sums $\sum_\alpha S_{\alpha,\pm}$ indeed vanish. As a result, (39) falls apart into one equation for $\hat{d}(z)$ plus two coupled equations for $\hat{\rho}_{12}(z)$ and $\hat{\rho}_{21}(z)$. From (36) we see that $d(t)$ now satisfies a Volterra equation of the second kind. In the literature[39] it is known as the renewal equation.

As a further simplification we replace the correlation functions $c'(t)$ and $c''(t)$ by simple exponential functions.[23] We take into account the initial condition $c''(0)=0$, which follows from (25). Our Ansatz is

$$c'(t) = Ae^{-\eta\gamma_{\|}t}, \qquad c''(t) = Bte^{-\theta\gamma_{\|}t} \tag{40}$$

where η and θ are dimensionless positive reals, and the time t must be positive. The constants A and B can be expressed in terms of physical parameters by returning to (31). We obtain

$$\begin{aligned} \left|\sum_\alpha V_{\alpha,12}\right|^2 A &= \tfrac{1}{4}\eta^{-1}\gamma_{\|}^2(\zeta^2+\eta^2) \\ \left|\sum_\alpha V_{\alpha,12}\right|^2 B &= -\tfrac{1}{4}(\theta\zeta)^{-1}d_\infty\gamma_{\|}^3(\zeta^2+\theta^2)^2 \end{aligned} \tag{41}$$

with the definitions $\zeta = \omega/\gamma_{\|}$ and $\omega = \omega_{12}$.

In practice, the correlation functions $c'(t)$ and $c''(t)$ do not decay exponentially fast. Nevertheless, it is instructive to work with the exponential fit (40). Since each Laplace transform is now a meromorphic function, the solutions for $\rho_{12}(t)$ and $d(t)$ can be calculated explicitly. This gives us some idea as to what kind of dynamical behavior we can expect from (36).

Employing the above-discussed assumptions, we find from (37) and (39)

$$\begin{aligned} \gamma_{\|}\hat{d}(\gamma_{\|}z) &= P^{-1}(z)[(z+i\eta)^2-\zeta^2]\left\{d(0)+\frac{\lambda^2 d_\infty(z+i\theta)(\zeta^2+\theta^2)^2}{z\theta[(z+i\theta)^2-\zeta^2]^2}\right\} \\ P(z) &= z^3+2i\eta z^2-(\zeta^2+\eta^2)(1+\lambda^2/\eta)z-i\lambda^2(\zeta^2+\eta^2) \end{aligned} \tag{42}$$

To determine the position of all poles of $\hat{d}(z)$ one must evaluate the roots of the polynomial $P(z)$. We do so for λ tending to zero, and subsequently calculate $\lim_{\lambda\to 0} d(t/\lambda^2)$. As expected, this yields the Markovian result for the inversion that was given under (6).

The atomic frequency defines a time scale ω^{-1} on which the experimentally observed inversion does not vary appreciably (see ref. 25, p. 47). Hence, in evaluating the zeros of $P(z)$ for finite λ one may treat ζ

as a parameter that tends to infinity. In leading order of ζ we obtain $z=\pm a\zeta-ib$ and $z=-ic$, with $a=(1+\lambda^2/\eta)^{1/2}$, $b=a^{-2}\eta(1+\frac{1}{2}\lambda^2/\eta)$, and $c=a^{-2}\lambda^2$. If both ζ and $\lambda^2\zeta$ tend to infinity, then the inversion comes out as

$$\begin{aligned} d(t)=d_\infty &+[d(0)-d_\infty(1+\lambda^2/\eta-\lambda^2/\theta)](1+\lambda^2/\eta)^{-1}\exp[-\gamma_{\|}\lambda^2 t/(1+\lambda^2/\eta)] \\ &+[d(0)\lambda^2/\eta+d_\infty\eta/\theta](1+\lambda^2/\eta)^{-1}\cos[(1+\lambda^2/\eta)^{1/2}\omega t] \\ &\times\exp[-\eta\gamma_{\|}t(1+\tfrac{1}{2}\lambda^2/\eta)/(1+\lambda^2/\eta)] \\ &+d_\infty\eta\theta^{-1}[\gamma_{\|}t(\theta-\eta)-1]\cos(\omega t)\exp(-\theta\gamma_{\|}t) \end{aligned} \tag{43}$$

Note that it is forbidden to take $\lambda\to 0$ in the above result. Often, experimental time resolution is insufficient to detect signals which oscillate with the atomic frequency ω. Then the last two contributions of (43) can be omitted. Phrased differently, for $t\geqslant T$ one may replace (43) by the Markovian evolution law

$$d(t)=d_\infty+[d(0)_{\text{eff}}-d_\infty]\exp(-\gamma_{\|,\text{eff}}t)$$

where the time T is of order ω^{-1}. The effective initial condition[10] and the effective relaxation constant are given by $d(0)_{\text{eff}}=[d(0)+d_\infty/\theta]\times(1+\eta^{-1})^{-1}$ and $\gamma_{\|,\text{eff}}=\gamma_{\|}(1+\eta^{-1})^{-1}$, respectively.

The result (43) corroborates the statement that for a quantum dissipative process one has to distinguish three time scales: the duration ω^{-1} of one atomic oscillation, the decay time τ_c of reservoir correlations, and the decay time $\gamma_{\|}^{-1}$ of observables. In standard experiments the three time scales are well separated from each other according to $\omega\gg\tau_c^{-1}\gg\gamma_{\|}$. These inequalities underlie the Markov approximation.[3,10,11,17] Within the framework of the exponential fit (40) the last remark can be proved explicitly. We have

$$\lim_{\lambda\to 0} d(t/\lambda^2)=\lim_{\zeta,\eta,\theta\to\infty} d(t)|_{\lambda=1} \tag{44}$$

where $d(t)$ must be evaluated on the basis of (42). The limit on the right-hand side should be taken such that it is the mathematical implementation of the above-given physical inequalities. Hence, one may choose $\zeta=\eta^2$, $\theta/\eta=\text{const}$, and let η go to infinity.

From (36) the conditions $d(t)|_{t=0}=d(0)$ and $\dot{d}(t)|_{t=0}=0$ are found. The result (43) obeys the first condition only. In order to remove this inconsistency we have to return to (42), and evaluate the inversion up to order ζ^{-1}. One arrives at a rather lengthy expression, which of course includes the complete right-hand side of (43). Now the time derivative is indeed zero at $t=0$.

To explain what is going on we take a look at the functions $g_n(t) = t - n^{-1}\sin(nt)$, with n a positive integer. These functions are encountered in order ζ^{-1}. At $t=0$ the derivative of $g_n(t)$ equals zero, but at the same time one has $g_\infty(t) = t$. Hence, as n increases, the time derivative tells us less and less about the function itself. For higher-order derivatives the situation is even worse. In conclusion, for large values of ζ there is no point in examining time derivatives of the density matrix. Results such as (34) are of little value then.

In Fig. 1 the inversion $d(t)$ as given by (43) is plotted against $\gamma_{\|}t$. The values of our parameters are $\zeta = 10$, $\eta = 1$, $\theta = 2$, and $\lambda = 1$. In Fig. 1a we have chosen $d(0) = 1/2$ and $d_\infty = -1/2$, so here a dissipative process takes place. The smooth curve corresponds to the Markovian result $d(t) = -1/2 + \exp(-\gamma_{\|}t)$. For $\gamma_{\|}t \geqslant 6$, oscillations in the curve (43) have damped out, and the distance to the Markovian curve is negligibly small. Note that for all times one has $|d(t)| \leqslant 1/2$. If $\rho_{12}(t) = 0$, this is precisely the von Neumann condition (7).

For the process described by Fig. 1b dissipation of the energy $\mathrm{Tr}[H_{\mathscr{S}}\rho_{\mathscr{S}}(t)]$ is absent, because we have chosen $d(0) = d_\infty = -1/2$. The curve generated by (43) oscillates around the straight line $d(t) = -1/2$,

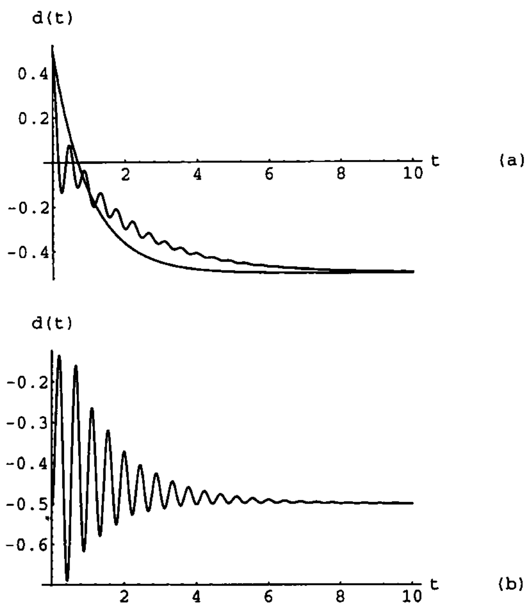

Fig. 1. Plots of the inversion (43) for $\zeta = 10$, $\eta = 1$, $\theta = 2$, and $\lambda = 1$. At the horizontal axes the time t is measured in units of $\gamma_{\|}^{-1}$. (a) $d(0) = 1/2$, $d_\infty = -1/2$; the smooth curve represents the Markovian result. (b) $d(0) = d_\infty = -1/2$.

which represents the Markovian result for the inversion. The oscillations go through minima which lie below $-1/2$, so the von Neumann condition (7) is violated. At first sight this seems to be strange, because Fig. 1b stands for a trivial process. However, because of the choice $d(0) = -1/2$, the exact inversion will take on values which are only marginally greater than $-1/2$. Hence, in approximating the exact density matrix (3) already a minor error can result into a contradiction with (7).

We repeat the calculation leading to (43) for the off-diagonal $\rho_{12}(t)$. Defining $\sum_\alpha V_{\alpha,12} = |\sum_\alpha V_{\alpha,12}| \exp(i\phi)$, we obtain

$$\begin{aligned}\rho_{12}(t) = {} & \tfrac{1}{2}\lambda^2\eta^{-1}[\rho_{12}(0) + \rho_{21}(0)\exp(2i\phi)] \\ & \times (1+\lambda^2/\eta)^{-1} \exp[-\eta\gamma_{\parallel} t/(1+\lambda^2/\eta)] \\ & + \tfrac{1}{2}A_+(1+\lambda^2/\eta)^{-1} \exp[-i(1+\lambda^2/\eta)^{1/2}\omega t - \tfrac{1}{2}\gamma_{\parallel}\lambda^2 t/(1+\lambda^2/\eta)] \\ & + \tfrac{1}{2}A_-(1+\lambda^2/\eta)^{-1} \exp[i(1+\lambda^2/\eta)^{1/2}\omega t - \tfrac{1}{2}\gamma_{\parallel}\lambda^2 t/(1+\lambda^2/\eta)] \end{aligned} \tag{45}$$

where we used the abbreviation

$$A_{\pm} = \rho_{12}(0)[1 \pm (1+\lambda^2/\eta)^{1/2} + \tfrac{1}{2}\lambda^2/\eta] - \tfrac{1}{2}\rho_{21}(0)\eta^{-1}\lambda^2 e^{2i\phi} \tag{46}$$

The result (45) is valid for all $\lambda \geqslant 0$ and obeys the constraint $\rho_{12}(t)|_{t=0} = \rho_{12}(0)$. As for the inversion, one can specify under which physical circumstances the weak-coupling limit may be taken. We have

$$\lim_{\lambda\to 0} e^{i\omega t/\lambda^2} \rho_{12}(t/\lambda^2) = \lim_{\zeta,\eta,\theta\to\infty} e^{i\omega t} \rho_{12}(t)|_{\lambda=1} \tag{47}$$

If we take the limit on the right-hand side in the same way as in (44), then for the off-diagonal $\rho_{12}(t)$ the expression (45) may be inserted. Use must be made of the relation $\omega_0 = \omega/(2\eta)$, which follows from (31) and (40).

6. EFFECTIVE RELAXATION CONSTANTS

In this section we aim at calculating effective values for the relaxation constants $\gamma_\perp$ and $\gamma_\parallel$ on the basis of the evolution equations (36) and the exponential fit (40). The diagonals $\{V_{\alpha,kk}\}$ are assumed to be nonzero. For a single two-level atom this is the case if a permanent electric dipole moment is present. For a gas of two-level atoms one may argue that collisions destroy any parity of the states $\{|1\rangle, |2\rangle\}$. In other words, by allowing the matrix elements $\{V_{\alpha,kk}\}$ to be nonzero, one phenomenologically takes into account collisional damping.

The solutions $\rho_{12}(t)$ and $d(t)$ of (36) are found by applying Cramers' rule to the matrix equation (39). Owing to the use of the exponential fit, the transforms $\hat{\rho}_{12}(z)$ and $\hat{d}(z)$ are everywhere analytic, except for a finite number of poles. One of these is located at $z=0$; its residue generates an asymptotic value, because one can write $\lim_{z\to 0} z\hat{f}(z) = \lim_{t\to\infty} f(t)$ whenever the right-hand side exists.

Under the inverse Laplace transformation each pole $z=u-iv$, with u and v real, gives rise to a factor $\exp(-iut-vt)$. Thus, all of our poles must have a negative imaginary part. The physically interesting poles lie directly below the real axis. They can be evaluated by solving for the zeros of the determinant D_c of the coefficient matrix of (39). The inequality $\eta, \theta \gg 1$ guarantees that all poles $z \neq 0$ for which D_c is nonzero lie far below the real axis.

The calculation of the determinant D_c is a technical job that is carried out in Appendix B. One obtains $D_c = P_{12}(z)/N(z)$, with

$$
\begin{aligned}
P_{12}(z) &= \sum_{n=0}^{12} a_n(-iz/\gamma_{\|})^n \\
\gamma_{\|}^3 N(\gamma_{\|} z) &= (z+i\eta)(z+i\theta)^2[(z+i\eta)^2-\zeta^2][(z+i\theta)^2-\zeta^2]^2
\end{aligned}
\tag{48}
$$

where the coefficients $\{a_n\}$ are real.

As discussed in Appendix B, for small coupling parameter λ two roots of the polynomial $P_{12}(z)$ are given by $z=-i\gamma_{\|}\lambda^2$ and $z=\omega+(\omega_0-i\gamma_{\perp})\lambda^2$. In the interaction picture these poles precisely generate the exponential factors $\exp(-\gamma_{\|}t)$ and $\exp[-(\gamma_{\perp}+i\omega_0)t]$, which are found upon solving (6). In order to derive this satisfactory result, one needs the relations

$$
\begin{aligned}
\Gamma &= \tfrac{1}{4}\eta^{-2}v_-^2(\zeta^2+\eta^2) \\
\omega_0 &= \tfrac{1}{2}\eta^{-1}\gamma_{\|}\zeta + \tfrac{1}{4}\zeta^{-1}\theta^{-3}\gamma_{\|}v_+v_-d_{\infty}(\zeta^2+\theta^2)^2
\end{aligned}
\tag{49}
$$

where we defined $v_{\pm} = \sum_\alpha (V_{\alpha,22} \pm V_{\alpha,11})/|\sum_\alpha V_{\alpha,12}|$. The result (49) follows from (31) and (40)–(41).

Taking λ finite again, we solve for the roots of P_{12}. As in Section 5, we let the parameter ζ go to infinity. One should be aware of the fact that the constant Γ and the ratio ω_0/ω must remain finite. Hence, we have to assume that both v_+ and v_- are of the order ζ^{-1} for large values of ζ. Without this assumption the exponential fit breaks down because of (49). In calculating the coefficients $\{a_n\}$ we first eliminate v_+ and v_- in favor of the parameter Γ and the ratio $q \equiv v_+/v_-$. Subsequently, we take ζ large. The results are presented in Appendix B.

If $z=w$ is a root of $P_{12}(z)$, then $z=-w^*$ is a root as well. For large values of ζ a root can behave in one of two ways: either it linearly depends on ζ according to $z/\gamma_{\|}=a\zeta+b$, or it remains finite in norm. The roots of the first type govern the time evolution of the function

$\exp(i\omega t)\,\rho_{12}(t)$. They can be used to calculate an effective value for the relaxation constant $\gamma_\perp$. The roots of the second type do not generate any rapidly oscillating factors $\exp(\pm i\omega t)$. They determine the evolution of the inversion $d(t)$, and therefore give rise to an effective value for the relaxation constant $\gamma_{\parallel}$.

We substitute the above-given linear form for $z/\gamma_{\parallel}$ into $P_{12}(z)$ and collect all terms which are of the same order in ζ. This yields the equation $P_{12}(z) = c_1\zeta^{12} + c_2\zeta^{11} + c_3\zeta^{10} + \cdots = 0$. Since ζ tends to infinity, each of the coefficients c_1, c_2, and c_3 must equal zero. From (B4) and the equation $c_1 = 0$ we find $a^2 = 1$ and $a^2 = 1 + \lambda^2/\eta$. Both solutions occur with a multiplicity of 2, so there exist eight poles of type 1.

From the equality $a^2 = 1$ we infer that the coefficient c_2 equals zero. The same is true for the equality $a^2 = 1 + \lambda^2/\eta$. In order to evaluate c_3, one has to calculate the coefficients $\{a_n\colon n = 2, 3, 5, 7, 9, 11, 12\}$ in leading order of ζ. Furthermore, for each of the coefficients $\{a_n\colon n = 4, 6, 8, 10\}$ one has to calculate the next-to-leading contribution as well. All of the corresponding expressions are listed under (B4).

The equality $c_3 = 0$ boils down to a quadratic equation for b. With the choice $a^2 = 1$ both solutions are given by $b = -i\theta$. The choice $a^2 = 1 + \lambda^2/\eta$ yields a more interesting result, namely

$$b = -\tfrac{1}{2} i\eta[1 \pm r/(1 + \lambda^2/\eta)] \tag{50}$$

The real root r is positive and defined as

$$r^2 = 1 + \Gamma\left[4d_\infty q\frac{\eta}{\theta} + \frac{\lambda^2}{\eta}\left(d_\infty q\frac{\eta}{\theta} - 2\right)\right]\left[2 - \frac{\lambda^2}{\eta}\left(d_\infty q\frac{\eta}{\theta} - 2\right)\right] \tag{51}$$

Note that Γ is of order η^{-2} because of the inequality $\zeta \gg \eta$ and the assumption $v_- \sim \zeta^{-1}$. Hence, the right-hand side of (51) is positive for η sufficiently large.

All poles of type 1 have now been evaluated. Two of them lie close to the real axis. They have the same imaginary part, which is found by choosing the minus sign in (50). Hence, we can introduce the following effective relaxation constant:

$$\gamma_{\perp,\mathrm{eff}} = \tfrac{1}{2}\gamma_{\parallel}\eta[1 - r/(1 + \lambda^2/\eta)] \tag{52}$$

where one should choose $\lambda = 1$. For η going to infinity the relaxation constant $\gamma_{\perp,\mathrm{eff}}$ converges to $\gamma_\perp$. Note that $\gamma_\perp$ equals $\gamma_{\parallel}/2$ because the constant Γ vanishes.

If the product $d_\infty q$ is positive, then root r has no upper bound. As a consequence, $\gamma_{\perp,\mathrm{eff}}$ can become negative. Accordingly, we have to restrict ourselves to the case $d_\infty q < 0$. Now one can write $r = (1-p)^{1/2}$, with p real and positive. For η sufficiently large and η/θ of order 1 we also have $p \leqslant 1$, so that $\gamma_{\perp,\mathrm{eff}}$ is real and positive.

The polynomial P_{12} possesses four roots of type 2. In leading order of ζ they satisfy the equation $\sum_{n=0}^{4} \lim_{\zeta\to\infty} (a_n/\zeta^8)(-iz/\gamma_{||})^n = 0$, which can be solved by means of standard formulas.[(40), 6] It turns out that for η, $\theta \gg 1$ all four roots lie on the negative imaginary axis. Only one root lies in the vicinity of the real axis. Hence, also for the relaxation constant $\gamma_{||}$ we can propose an effective value. Up to order η^{-3} it is given by

$$\gamma_{||,\mathrm{eff}} = \frac{\gamma_{||}\lambda^2}{1+\lambda^2/\eta} - \eta^{-1}\gamma_{||}\Gamma d_\infty q \lambda^4(1+2d_\infty q) \tag{53}$$

where λ should equal 1. We have set η equal to θ. In many cases the second term on the right-hand side may be neglected. For $\lambda = 1$ and η going to infinity the relaxation constant $\gamma_{||,\mathrm{eff}}$ converges to $\gamma_{||}$.

Since $|1\rangle$ is the ground state of our two-level system, it is reasonable to assume that $V_{\alpha,11} = 0$ for all α. We put d_∞ equal to $-1/2$, λ equal to 1, η equal to θ, and define $\kappa = \zeta v_-$. Then Eqs. (52) and (53) reduce to

$$\gamma_{\perp,\mathrm{eff}} = \frac{1}{2}\gamma_{||}\left\{\eta - \frac{[\eta^4 - \kappa^2(\eta+5/4)^2]^{1/2}}{1+\eta}\right\}, \qquad \gamma_{||,\mathrm{eff}} = \frac{\gamma_{||}}{1+1/\eta} \tag{54}$$

The square root is real and positive for $\eta > \eta_0$, with $2\eta_0 = |\kappa| + (\kappa^2 + 5|\kappa|)^{1/2}$. Because of the remark right below (8), the ratio $\delta_{\mathrm{eff}} \equiv \gamma_{||,\mathrm{eff}}/\gamma_{\perp,\mathrm{eff}}$ should be smaller than 2. For $\eta = \eta_0$ this is indeed true. If $|\kappa| > \sqrt{2}$, then δ_{eff} converges to 2 from below as η becomes large.

We compare the ratios δ_{eff} and $\delta \equiv \gamma_{||}/\gamma_\perp$ with each other. Since ζ is large, the latter can be written as

$$\delta = \frac{2}{1+\kappa^2/(2\eta^2)} \tag{55}$$

We choose $\Gamma = 10/\eta^2$, so that $\kappa^2 = 40$. The question arises of what values of η are physical. One can use the criterion that all of the physically irrelevant poles must lie below the line $z''/\gamma_{||} = -20$. This is true if η is slightly larger than 20.

As can be seen from Table I, for $20 \leqslant \eta \leqslant 100$ the values of δ_{eff} are markedly different from those of δ. For a two-level atom ζ is of order 10^8 (ref. 25, p. 47), so all η values of Table I satisfy the inequality $\zeta \gg \eta$ very well. The ratio $|\sum_\alpha V_{\alpha,22}/\sum_\alpha V_{\alpha,12}|$ is equal to $\sqrt{40}\cdot 10^{-8}$.

[6] For $\eta = \theta$ one solution is given by $z = -i\eta\gamma_{||}$.

Table I. The Ratios δ_{eff} and δ as a Function of the Parameter η for $d_\infty = -1/2$, $\lambda = q = 1$, $\kappa^2 = 40$, and $\eta = \theta$

η	δ_{eff}	δ
20	0.925	1.905
30	1.155	1.957
40	1.303	1.975
50	1.406	1.984
100	1.659	1.996
1000	1.961	2.000

Upon increasing $|\kappa|$, differences between the effective relaxation constants and their Markovian counterparts become even more pronounced. Take $\kappa = 100$; then for $\eta \geqslant 5000$ the ratio δ is greater than $2 - 10^{-3}$. On the other hand, for $\eta = 5000$ the ratio δ_{eff} is equal to 1.000, and for η as big as 10^5 its value merely amounts to 1.905.

The above findings certainly are of experimental relevance. At the same time, we must remember that the quantity δ_{eff} has been calculated on the basis of the approximate master equation (36) and the exponential fit (40). Furthermore, we should be cautions if it comes to identifying the dynamics of the system $\mathscr{S}$ with the physics that is observed. Our reduced density matrix describes the time evolution of a microscopic entity such as a two-level atom. In experiments one usually measures macroscopic quantities, e.g., the induced polarization of a gas of 10^{23} molecules. The road from our one-particle theory to experimental reality is a long one. Several tough problems must be overcome, for instance, interactions between particles, damping through collisions, and inhomogeneous effects such as Doppler broadening.

7. CONCLUSION

The quantum mechanical description of dissipative processes on the basis of non-Markovian master equations constitutes a complicated topic in statistical physics. In this article we studied the issue at three different levels. First of all, some rigorous results were established. They respect the basic laws of quantum mechanics.

In Section 3 we constructed the inverse of the quantum dynamical map that governs the evolution of the reduced density operator. This enables one to cast the old Nakajima–Zwanzig equation in a form which is local in time. Furthermore, we combined perturbative methods with projection techniques so as to derive a modified Nakajima–Zwanzig equation. Up to nth order in the coupling parameter λ the new equation contains all terms out of the perturbation expansion for the reduced density operator. The character n stands for any positive integer.

Both the modified and the standard Nakajima–Zwanzig equation are formal identities which essentially represent an infinite hierarchy of equations. Hence, in order to perform practical calculations at finite values of the coupling parameter, one is forced to leave the rigorous level. At this point the modified Nakajima–Zwanzig equation proves its value. If we drop one single contribution, then we obtain a non-Markovian master equation that lends itself to practical applications.

Of course, the solution of the new equation does not coincide with the exact reduced density operator. However, through the integer n one has complete control over the corresponding error. Moreover, the error converges to zero if the weak-coupling limit is taken. Because of these facts, the modified Nakajima–Zwanzig equation should provide an excellent basis for performing exact numerical work on the evolution of open quantum systems.

For n equal to unity our approximate master equation reduces to the simplest non-Markovian evolution equation one can think of.[13,16] It can be directly found from the Nakajima–Zwanzig equation by discarding all reservoir correlation functions of order three and higher, as well as all products of correlation functions. In Section 4 we investigated whether the simplest non-Markovian master equation can furnish predictions which are physically relevant. Particular attention was paid to the von Neumann conditions.

Focusing on a two-level system, we demonstrated that both for small and for large times the von Neumann conditions are not seriously violated. For an N-level system we proved explicitly that in the weak-coupling limit the solution of the simplest non-Markovian master equation no longer differs from the exact reduced density operator. As a byproduct of the proof one finds an interesting statement on the conditions under which the weak-coupling limit may be taken in the Nakajima–Zwanzig equation. The standard conditions as given in the literature are insufficient if the Hilbert space for the system is of infinite dimension, and if the potential describing the interaction between system and reservoir is an infinite sum of product operators.

In Sections 5 and 6 we descended to a completely phenomenological level. In the simplest non-Markovian master equation the correlation functions of the reservoir were replaced by exponential functions. The amplitudes of these functions were expressed in terms of physical parameters by making use of the weak-coupling limit. Within the framework of this exponential fit we found a physical limit which is fully equivalent to the weak-coupling limit. Again we specialized to a two-level system.

The exponential fit allows us to derive the Bloch equations from the simplest non-Markovian master equation at a fixed value of the coupling parameter. In the ensuing Bloch equations the rate of dissipation is determined by effective relaxation constants $\gamma_{\perp,\text{eff}}$ and $\gamma_{\parallel,\text{eff}}$, which explicitly depend on the correlation time of the reservoir. Under normal physical circumstances the effective constants can differ from their Markovian counterparts $\gamma_\perp$ and $\gamma_\parallel$ by no less than 50%. Findings such as these suggest that one should undertake further investigations. For instance, the dynamics of the simplest non-Markovian master equation could be studied for more realistic choices of the correlation functions. Also, one might attempt to carry out analytic work for master equations of higher order.

APPENDIX A. THE WEAK-COUPLING LIMIT FOR $A_{00} = A_{11} = 0$

We shall demonstrate that for λ tending to zero the matrix $\rho_{\mathscr{S}}^{(1)}(t/\lambda^2)$ satisfies a Markovian master equation, the generator of which is given by (29). We remark that this appendix may very well serve as an introduction to the important work of Davies.[14,19]

Let us introduce the linear space $\mathscr{C}[0, a]$ of continuous functions with domain $[0, a]$ and range in $\mathscr{M}$. If the norm $\|M\|_{\mathscr{C}} = \sup_{0 \leqslant t \leqslant a} \|M(t)\|$ is used, then $\mathscr{C}$ is a Banach space (ref. 29, p. 27). As already discussed, (26) may be iterated *ad infinitum*. The result reads

$$\rho_{\mathscr{S}}^{(1)}(t/\lambda^2) = \rho_{\mathscr{S}} + \sum_{n=1}^{\infty} (\mathscr{L}_\lambda^n \rho_{\mathscr{S}})(t) \equiv \phi_\lambda(t) \tag{A1}$$

with $t \in [0, a]$ and $\lambda > 0$. The series on the right-hand side converges in the norm on $\mathscr{C}$. The operator $\mathscr{L}_\lambda$: $\mathscr{C} \to \mathscr{C}$ is bounded and defined as

$$(\mathscr{L}_\lambda M)(t) = \int_0^t ds\, L\left(\frac{t-s}{\lambda^2}, \frac{s}{\lambda^2}\right) M(s) \tag{A2}$$

where $M(t)$ belongs to $\mathscr{C}$.

Under the use of induction, the assumptions (28) lead to the following inequality:

$$\|\mathscr{L}_\lambda^n M\|_{\mathscr{C}} \leqslant \frac{(ah)^n}{n!} \|M\|_{\mathscr{C}} \tag{A3}$$

with λ and n positive. The constant h equals $4cv^2$. Since $\mathscr{M}$ is a complete space, the assumptions (28) also imply that for $j = 1, 2, 3, 4$ and all $M \in \mathscr{M}$

the matrix $L_j(t, s)M$ converges to an element of $\mathscr{M}$ as t becomes large. The new matrix will be called $L_j(\infty, s)M$. For all $s \geqslant 0$ the operator $L(\infty, s) \equiv \sum_{j=1}^{4} L_j(\infty, s)$ is bounded with respect to the norm on $\mathscr{M}$.

Because of the fact that $L(\infty, t/\lambda^2)\, M(t)$ belongs to $\mathscr{C}$ for each $M(t) \in \mathscr{C}$, we can define the bounded operator $\mathscr{K}_\lambda$: $\mathscr{C} \to \mathscr{C}$ as follows:

$$(\mathscr{K}_\lambda M)(t) = \int_0^t ds\, L\left(\infty, \frac{s}{\lambda^2}\right) M(s) \tag{A4}$$

with λ positive. The equality (A3) remains true if $\mathscr{L}_\lambda$ is replaced by the operator $\mathscr{K}_\lambda$. Hence, by completeness of $\mathscr{C}$ we find that for all $\lambda > 0$ the sum

$$\chi_\lambda(t) \equiv \rho_{\mathscr{S}} + \sum_{n=1}^{\infty} (\mathscr{K}_\lambda^n \rho_{\mathscr{S}})(t) \tag{A5}$$

represents an element of $\mathscr{C}$.

Use of the operator identity

$$A^n - B^n = \sum_{r=0}^{n-1} A^r(A-B)\, B^{n-1-r} \tag{A6}$$

with n a positive integer, as well as relations (A1) and (A5), brings us to the following inequality (ref. 14, p. 141):

$$\|\phi_\lambda - \chi_\lambda\|_{\mathscr{C}} \leqslant e^{2ah}\, \|\rho_{\mathscr{S}}\|\ \|\mathscr{L}_\lambda - \mathscr{K}_\lambda\| \tag{A7}$$

with $\lambda > 0$. The operator norm on the right-hand side is the sup-norm on the space $\mathscr{C}$. From (28) and the definition of $L(\infty, t)$ one deduces that

$$\|\mathscr{L}_\lambda - \mathscr{K}_\lambda\| \leqslant 4v^2 \sup_{0 \leqslant t \leqslant a} \int_0^t ds\, p\left(\frac{t-s}{\lambda^2}\right) \leqslant 4v^2 \lambda^{1/2} p(0) + 4v^2(a - \lambda^{1/2})\, p(\lambda^{-3/2}) \tag{A8}$$

We have made use of the definition

$$p(t) = \sup_{\alpha\beta} \int_t^{\infty} ds\, |c_{\alpha\beta}(s)| \tag{A9}$$

so that $p(0) = c$. To derive the second inequality of (A8) one must carry out the transformation $s \to t - s$ and divide the integration interval into the two parts $[0, \lambda^{1/2}]$ and $[\lambda^{1/2}, a]$.

Since the Hilbert space $\mathscr{H}_{\mathscr{S}}$ is of finite dimension, the parameters α and β go through a finite number of values. Hence, (28) implies that

$\lim_{t\to\infty} p(t) = 0$. Consequently, the right-hand side of (A8) goes to zero for $\lambda \to 0$. We therefore arrive at

$$\lim_{\lambda \to 0} \|\phi_\lambda - \chi_\lambda\|_{\mathscr{C}} = 0 \tag{A10}$$

The following should be emphasized. If α and β can take on infinitely many values, then (28) does not say anything about the asymptotic behavior of the function $p(t)$. Choose, for instance, $c_j(t) = j/(j^2 + t^2)$. Now $p(0)$ exists, but at the same time one has $p(\infty) = \pi/2 \neq 0$. Hence, the standard[4, 9, 35] conditions for deriving the weak-coupling limit apply to the case in which the sum (24) is finite.

We still have to prove that χ_λ converges to an element of $\mathscr{C}$ if λ becomes small. Because of the equality $\lim_{b\to\infty} b^{-1} \int_0^b ds \exp(i\omega s) = \delta(\omega, 0)$, one can prove for each $M \in \mathscr{M}$ and $x, y \in \mathbf{C}^N$ the identity

$$\lim_{b \to \infty} \left\langle x, \left(b^{-1} \int_0^b ds\, L(\infty, s)\, M\right) y \right\rangle = \langle x, (L_0 M)\, y\rangle \tag{A11}$$

where $\langle \cdot, \cdot \rangle$ denotes the inner product on $\mathbf{C}^N$. We have used the definition (29) of L_0 and the fact that $\varepsilon_k = \varepsilon_l$ iff $k = l$.

Since $\mathscr{M}$ is of finite dimension, identity (A11) implies that the matrix $b^{-1} \int_0^b ds\, L(\infty, s) M$ converges in norm to the matrix $L_0 M$ as b becomes large. By using $\dim(\mathscr{M}) < \infty$ again, we see that one may even write $\lim_{b\to\infty} \|J_b\| = 0$, with $J_b \equiv b^{-1} \int_0^b ds\, L(\infty, s) - L_0$, and $\|\cdot\|$ the sup-norm on $\mathscr{M}$.

The operator $\mathscr{K}: \mathscr{C} \to \mathscr{C}$ is defined by $(\mathscr{K} M)(t) \equiv \int_0^t ds\, L_0 M(s)$. Upon replacing in (A3) the operator $\mathscr{L}_\lambda$ by $\mathscr{K}$ and the real number h by $\|L_0\|$, we obtain an inequality that is true. Therefore, the sum $\sigma(t) \equiv \rho_{\mathscr{S}} + \sum_{n=1}^\infty (\mathscr{K}^n \rho_{\mathscr{S}})(t)$ represents an element of $\mathscr{C}$. It obeys the following Markovian master equation:

$$\sigma(t) = \rho_{\mathscr{S}} + \int_0^t ds\, L_0 \sigma(s) \tag{A12}$$

From (A6) one finds for all positive integers n the result

$$\begin{aligned} \|\chi_\lambda - \sigma\|_{\mathscr{C}} \leqslant{}& \sum_{m=1}^{n} \sum_{r=0}^{m-1} \frac{(ah)^r}{r!} \|(\mathscr{K}_\lambda - \mathscr{K})\, \mathscr{K}^{m-1-r} \rho_{\mathscr{S}}\|_{\mathscr{C}} \\ &+ 2\, \|\rho_{\mathscr{S}}\| \sum_{m=n+1}^{\infty} [\max(h, \|L_0\|)\, a]^m / m! \end{aligned} \tag{A13}$$

It follows that the norm $\|\chi_\lambda - \sigma\|_{\mathscr{C}}$ goes to zero for $\lambda \to 0$ if $\lim_{\lambda \to 0} \|(\mathscr{K}_\lambda - \mathscr{K})M\|_{\mathscr{C}} = 0$ for all $M(t) \in \mathscr{C}$ which possess a time derivative $\dot{M}(t) \in \mathscr{C}$.

Via two partial integrations we obtain from the definitions of the operators $\mathscr{K}_\lambda$ and $\mathscr{K}$ the identity (ref. 14, p. 132)

$$[(\mathscr{K}_\lambda - \mathscr{K})M](t) = tJ_{t/\lambda^2}M(t) - \int_0^t ds\, sJ_{s/\lambda^2}\dot{M}(s) \tag{A14}$$

It gives rise to the inequality

$$\|(\mathscr{K}_\lambda - \mathscr{K})M\|_{\mathscr{C}} \leqslant (\|M\|_{\mathscr{C}} + a\,\|\dot{M}\|_{\mathscr{C}}) \sup_{0 \leqslant t \leqslant a} \|tJ_{t/\lambda^2}\| \tag{A15}$$

Divide the interval $[0, a]$ into the two parts $[0, \lambda]$ and $[\lambda, a]$. By employing the assumptions (28) we end up with

$$\sup_{0 \leqslant t \leqslant a} \|tJ_{t/\lambda^2}\| \leqslant \lambda(4cv^2 + \|L_0\|) + a \sup_{\lambda^{-1} \leqslant \tau \leqslant a\lambda^{-2}} \|J_\tau\| \tag{A16}$$

Since $\|J_\tau\|$ is continuous in τ, the supremum on the right-hand side of (A16) may be replaced by the norm $\|J_{\tau(\lambda)}\|$, with $\tau(\lambda)$ a real number satisfying $\tau(\lambda) \geqslant \lambda^{-1}$. Consequently, the right-hand side of (A15) vanishes if λ goes to zero. In other words, we have proved the equality $\lim_{\lambda \to 0} \|\chi_\lambda - \sigma\|_{\mathscr{C}} = 0$. Together with (A10), it leads us to the following final result:

$$\lim_{\lambda \to 0} \sup_{0 \leqslant t \leqslant a} \|\rho_{\mathscr{S}}^{(1)}(t/\lambda^2) - \sigma(t)\| = 0 \tag{A17}$$

The constant a is positive, and the matrix $\sigma(t)$ satisfies the master equation (A12).

APPENDIX B. CALCULATION OF DETERMINANT D_c

In the main text we defined D_c to be the determinant of the coefficient matrix of (39). Denoting the Laplace transforms of $c'(t)$ and $c''(t)$ by $r(z)$ and $s(z)$, respectively, and combining the assumption $c_{\alpha\beta}(t) = c(t)$ with (37), we arrive at

$$D_c = z^3 - u^2\lambda^2 z^2 A_1(z) - \omega^2 z + \omega u^2 \lambda^2 z A_2(z) + u^4 \lambda^4 z A_3(z)$$
$$+ 2\omega^2 u^2 \lambda^2 A_4(z) + 2\omega u^4 \lambda^4 A_5(z) \tag{B1}$$

with

$$A_1(z) = (2+v_-^2)[r(z+\omega)+r(z-\omega)] + 4r(z) + iv_+v_-[s(z+\omega)-s(z-\omega)]$$
$$A_2(z) = v_-^2[r(z+\omega)-r(z-\omega)] + iv_+v_-[s(z+\omega)+s(z-\omega)]$$
$$\begin{aligned} A_3(z) = {} & (4v_-^2+v_-^4)\, r(z+\omega)\, r(z-\omega) + v_+^2 v_-^2 s(z+\omega)\, s(z-\omega) \\ & + iv_+v_-(2+v_-^2)[r(z-\omega)\, s(z+\omega) - r(z+\omega)\, s(z-\omega)] \\ & + 2(4+v_-^2)\, r(z)[r(z-\omega)+r(z+\omega)] \\ & + 2iv_+v_-r(z)[s(z+\omega)-s(z-\omega)] \\ & + 2iv_+v_-s(z)[r(z-\omega)-r(z+\omega)] + 2v_+^2 s(z)[s(z+\omega)+s(z-\omega)] \end{aligned}$$
$$A_4(z) = r(z+\omega) + r(z-\omega)$$
$$\begin{aligned} A_5(z) = {} & v_+^2 s(z)[s(z-\omega)-s(z+\omega)] + iv_+v_-s(z)[r(z+\omega)+r(z-\omega)] \\ & - iv_+v_-[r(z+\omega)\, s(z-\omega) + r(z-\omega)\, s(z+\omega)] \end{aligned} \tag{B2}$$

We defined $u = |\sum_\alpha V_{\alpha,12}|$, and $v_\pm = \sum_\alpha S_{\alpha,\pm}/u$. Note that in the course of calculating D_c one meets contributions which contain λ^6 as a factor. They add up to zero.

By employing the exponential fit (40)–(41) we obtain

$$u^2 r(z) = \frac{\gamma_{\|}(\zeta^2+\eta^2)}{4\eta(z/\gamma_{\|}+i\eta)}, \qquad u^2 s(z) = \frac{\gamma_{\|} d_\infty (\zeta^2+\theta^2)^2}{4i\zeta\theta(z/\gamma_{\|}+i\theta)^2} \tag{B3}$$

The evaluation of the coefficients $\{a_n\}$ as defined in (48) is now a matter of tedious algebra. Use should be made of the fact that the parameter ζ is large. As explained in the main text, one must assume that v_+ and v_- both are of order ζ^{-1}.

All coefficients have been evaluated in leading order of ζ; for some coefficients the next order has been evaluated as well. We have employed relation (49) and the definition $q = v_+/v_-$. The results are given by

$$a_{12} = 1, \qquad a_{11} = 3\eta + 6\theta$$
$$a_{10} = \zeta^2[4 + 2\eta^{-1}\lambda^2] + 3\eta^2 + 18\eta\theta + 15\theta^2 + 2\eta\lambda^2(1+\Gamma)$$
$$a_9 = \zeta^2[10\eta + 20\theta + 4\eta^{-1}\lambda^2(\eta+3\theta)] + \mathcal{O}(\zeta^0)$$
$$\begin{aligned} a_8 = {} & \zeta^4[6 + 6\eta^{-1}\lambda^2 + \eta^{-2}\lambda^4] \\ & + \zeta^2[9\eta^2 + 48\eta\theta + 42\theta^2 + \eta^{-1}\lambda^2(8\eta^2 + 24\eta\theta + 30\theta^2 + 2\eta^2\Gamma \\ & + 6d_\infty q\eta^3\theta^{-1}\Gamma) + 2\lambda^4(1+\Gamma)] + \mathcal{O}(\zeta^0) \end{aligned}$$
$$a_7 = \zeta^4[12\eta + 24\theta + \eta^{-1}\lambda^2(10\eta + 28\theta) + \eta^{-2}\lambda^4(\eta + 6\theta)] + \mathcal{O}(\zeta^2)$$

$$
\begin{aligned}
a_6 = {} & \zeta^6[4 + 6\eta^{-1}\lambda^2 + 2\eta^{-2}\lambda^4] \\
& + \zeta^4[9\eta^2 + 44\eta\theta + 40\theta^2 + \eta^{-1}\lambda^2(11\eta^2 + 44\eta\theta + 54\theta^2 - 2\eta^2\Gamma \\
& + 4d_\infty q\eta^3\theta^{-1}\Gamma) + \eta^{-2}\lambda^4(4\eta^2 + 6\eta\theta + 15\theta^2 + 4\eta^2\Gamma \\
& + 2d_\infty q\eta^3\theta^{-1}\Gamma + d_\infty^2 q^2\eta^4\theta^{-2}\Gamma)] + \mathcal{O}(\zeta^2) \\
a_5 = {} & \zeta^6[6\eta + 12\theta + \eta^{-1}\lambda^2(8\eta + 20\theta) + \eta^{-2}\lambda^4(2\eta + 8\theta)] + \mathcal{O}(\zeta^4) \\
a_4 = {} & \zeta^8[1 + \eta^{-1}\lambda^2]^2 + \zeta^6[3\eta^2 + 16\eta\theta + 14\theta^2 \\
& + \eta^{-1}\lambda^2(6\eta^2 + 24\eta\theta + 26\theta^2 - 2\eta^2\Gamma - 2d_\infty q\eta^3\theta^{-1}\Gamma) \\
& + 2\eta^{-2}\lambda^4(\eta^2 + 4\eta\theta + 6\theta^2 + \eta^2\Gamma - d_\infty^2 q^2\eta^4\theta^{-2}\Gamma)] + \mathcal{O}(\zeta^4) \\
a_3 = {} & \zeta^8[1 + \eta^{-1}\lambda^2]^2(\eta + 2\theta) + \mathcal{O}(\zeta^6) \\
a_2 = {} & \zeta^8[2\eta\theta + \theta^2 + \eta^{-1}\lambda^2(\eta^2 + 4\eta\theta + 2\theta^2) + \theta\eta^{-2}\lambda^4(2\eta + \theta - 2d_\infty q\eta^3\theta^{-2}\Gamma \\
& - 3d_\infty^2 q^2\eta^4\theta^{-3}\Gamma)] + \mathcal{O}(\zeta^6) \\
a_1 = {} & \zeta^8\{\eta\theta^2 + 2\theta\lambda^2(\eta + \theta) + \theta^2\eta^{-1}\lambda^4[1 - 3d_\infty q\eta^3\theta^{-3}\Gamma \\
& - (3 + 2\eta^{-1}\theta)\, d_\infty^2 q^2\eta^4\theta^{-4}\Gamma]\} + \mathcal{O}(\zeta^6) \\
a_0 = {} & \zeta^8[\eta\theta^2\lambda^2 - d_\infty q\eta^3\theta^{-1}\Gamma\lambda^4(1 + 2d_\infty q)]
\end{aligned}
\tag{B4}
$$

We always choose $\Gamma > 0$, so v_- cannot equal zero. This implies that the ratio q is always finite.

In Section 6 we claimed that for λ close to zero the equation $P_{12}(z) = 0$ precisely yields the poles of the weak-coupling limit. This statement can be proved by substituting in the aforementioned equation $z/\gamma_{\parallel} = a\lambda^2$ and dropping all terms of order λ^4 and higher. One finds $a = -i$, even if the coefficients (B4) are used. To calculate the second pole one has to start from the full expression for P_{12}, i.e., the coefficients (B4) can no longer be employed. Carry out the substitution $z/\gamma_{\parallel} = \zeta + b\lambda^2$ and drop again all terms of order λ^4 and higher. The terms of order λ^0 cancel. One ends up with

$$
\begin{aligned}
P_{12} = {} & \{-2i\eta\theta^2\lambda^2\zeta^2 b + (\eta + i\zeta)\,\theta^2\lambda^2\zeta^2 + \tfrac{1}{2} i d_\infty v_+ v_- \eta\theta^{-1}\lambda^2\zeta(\zeta^2 + \theta^2)^2 \\
& + \tfrac{1}{2} v_-^2 \eta^{-1}\theta^2\lambda^2\zeta^2(\zeta^2 + \eta^2)\}\, Q
\end{aligned}
\tag{B5}
$$

where Q stands for the following polynomial:

$$
\begin{aligned}
Q = {} & 8\zeta^6 + i\zeta^5(12\eta + 24\theta) - \zeta^4(4\eta^2 + 36\eta\theta + 26\theta^2) \\
& - i\zeta^3(12\eta^2\theta + 39\eta\theta^2 + 12\theta^3) \\
& + \zeta^2(13\eta^2\theta^2 + 18\eta\theta^3 + 2\theta^4) + i\zeta(6\eta^2\theta^3 + 3\eta\theta^4) - \eta^2\theta^4
\end{aligned}
\tag{B6}
$$

If we put the right-hand side of (B5) equal to zero, then we find the second pole that was given below (48).

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