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Staying positive: going beyond Lindblad with perturbative master equations

Robert S Whitney

Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, France

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Abstract

The perturbative master equation (Bloch–Redfield) is used extensively to study dissipative quantum mechanics—particularly for qubits—despite the 25-year-old criticism that it violates positivity (generating negative probabilities). We take an arbitrary system coupled to an environment containing many degrees-of-freedom and cast its perturbative master equation (derived from a perturbative treatment of Nakajima–Zwanzig or Schoeller–Schön equations) in the form of a Lindblad master equation. We find that the equation's parameters are *time dependent*. This time dependence is rarely accounted for and invalidates Lindblad's dynamical semigroup analysis. We analyse one such Bloch–Redfield master equation (for a two-level system coupled to an environment with a short but non-vanishing memory time), which apparently violates positivity. We analytically show that, once the time dependence of the parameters is accounted for, positivity is preserved.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

No system is truly isolated from its environment, thus all quantum systems experience some amount of dissipation and decoherence [1, 2]. To understand the properties of real quantum systems we must understand the effect of dissipation in quantum mechanics. This is extremely relevant to recent works on qubits and quantum information processing (quantum computing and communication). In experiments [3–5], the coupling to the environment is typically not as small as would be required to build a quantum computer. One must understand the effect of the environment on a qubit, if one wishes to minimize it.

Any theory for a quantum system which exchanges energy and information (but not particles) with its environment should give a master equation (evolution equation) for the

system's density matrix which satisfies three basic requirements:

(i) preserves the hermiticity of the density matrix, so all probabilities are real,

(ii) preserves the trace of the density matrix, then the sum of probabilities over any complete set of orthogonal states is one,

(iii) preserves *positivity*. A system is positive only if the probability of *all* possible states is positive. Given (ii), this guarantees that all probabilities lie between zero and one. In this work we do not consider *complete positivity*, excepting comments in sections 2 and 7.

There are only a small number of models for which such master equations can be derived exactly (we will not address these here). In all other cases, there are two main methods for finding such a master equation [2]:

- *Phenomenological method.* Here one attempts to construct general master equations which satisfy requirements (i)–(iii). Under the assumption that the evolution is translationally invariant in time (a dynamical semigroup property), as is often the case for Markovian evolution, Lindblad [7, 8] considered the master equation given in equations (1*a*) and (1*b*). He proved that it is the *most general* equation that satisfies (i) and (ii), while also preserving complete positivity. *Complete positivity* is as strong or stronger than *positivity*, thus it automatically satisfies (iii) (see the comment in section 7 due to [6]).
- *Perturbative method* [1]. Here one takes the evolution of a system and its environment (from their combined Hamiltonian) and traces over the environment degrees-of-freedom. Various methods of doing this exist: Bloch–Redfield [9, 10], Nakajima–Zwanzig [11, 12] and Schoeller–Schön [13]. However one is typically forced to treat the system–environment interaction perturbatively, then all these approaches reduce to Bloch–Redfield's.

The Lindblad master equation (the most general generator of a dynamical semigroup) takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\mathrm{i}[\mathcal{H}_{\mathrm{sys}}, \hat{\rho}(t)]_- - \sum_{n=1}^{N^2-1} \frac{\lambda_n}{2}\left(\hat{L}_n^\dagger \hat{L}_n \hat{\rho}(t) + \hat{\rho}(t)\hat{L}_n^\dagger \hat{L}_n - 2\hat{L}_n \hat{\rho}(t) \hat{L}_n^\dagger\right), \tag{1a}$$

with

$$\lambda_n \geqslant 0 \qquad \text{for all} \quad n, \tag{1b}$$

where the commutator $[\hat{A}, \hat{B}]_- = \hat{A}\hat{B} - \hat{B}\hat{A}$ and $\{\hat{L}_n\}$ is a set of orthonormal (*trace-class*) operators. It is often assumed that all *Markovian* master equations fall into the category of dynamical semigroup evolution, and thus equations (1*a*) and (1*b*) give the most general Markovian evolution. However this is a subtle point, we discuss it (and define terms like 'dynamical semigroup' and 'trace-class') in section 2.

The perturbative method's advantage over the phenomenological method is that one can study how a particular environment (with a given spectrum, temperature, etc) affects the system. Thus one can address a crucial aspect of qubit research: how should one engineer a particular system to minimize decoherence? However the resulting Bloch–Redfield master equation has long been criticized [14, 15], because it can be written in the form in equation (1*a*) but then typically violates equation (1*b*). In these cases it violates Lindblad's condition for complete positivity. Further, there is plenty of evidence that it also violates positivity (see section 1.2).

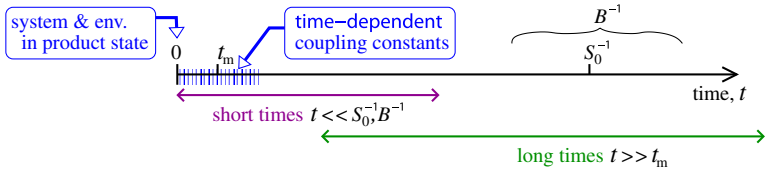

Figure 1. Timescales for the model (in section 6) for which we show positivity, despite it not satisfying Lindblad's requirement, equation (1*b*). The system is a spin-half with Hamiltonian $-\frac{1}{2}B\hat{\sigma}_z$, and the environment couples to the spin via $\hat{\sigma}_x$. The environment's noise spectrum (with noise power S_0) is broad, leading to a short memory time, t_m. Decoherence and relaxation times (both $\sim S_0^{-1}$) can be smaller or larger than the Larmor precession period, B^{-1}.

1.1. Outline of this paper

The objective of this paper is to study this apparent contradiction between the perturbative method and Lindblad's proof. We start by discussing, in section 2, the assumptions that underlie the Lindblad master equation. In section 3 we consider the Bloch–Redfield equation for an arbitrary system and show that, in general, one coupling constant, λ_2, is negative. However we also show that the parameters of the Bloch–Redfield master equation, $\{\lambda_n\}$ and $\{\hat{L}_n\}$, are *time dependent*. This means the master equation does not generate a dynamical semigroup. Thus Lindblad's proof is inapplicable to the Bloch–Redfield equation, and *a priori* we do not know whether a negative λ_2 will lead to a violation of positivity or not.

In section 6, we consider the Bloch–Redfield equation for a particular system (a two-level system coupled to an environment with a very broad spectrum of excitations). We divide the evolution into two overlapping regimes: short and long times (sketched in figure 1). The time dependence of the parameters is only relevant in the short-time regime (t much less than decoherence/relaxation times). We analytically show that the system remains positive in both regimes (i.e. for all $t \geqslant 0$), despite the negative coupling constant, λ_2.

1.2. The place of this work in the literature

In traditional derivations of the Bloch–Redfield master equation [1, 2], it is assumed that the parameters of the master equation are time independent. In reality all environment-induced terms in the master equation are zero at $t = 0$ (defined as the time at which the system and environment are in a factorized state), before growing with t and saturating at $t \gg t_m$, where t_m is the environment memory time. So, the assumption of time independence is *flawed* for times of order the memory time, t_m. This has been discussed in the context of coupled classical oscillators [16], over-damped Brownian motion [17], damped quantum oscillators [18–21][1], dissipative two-level systems [20, 22–24] and more generally [25, 26]. Nearly all these works consider dynamics on times of order t_m as an *initial slip*, after which the dynamics is given by the time-independent master equation, the justification for this is sketched in appendix B. Of most relevance to us are those works which try to show that positivity is preserved in this context [20–24, 26]. However these works provide only plausibility arguments[2] or

[1] References [19, 28] consider *non*-Lindblad master equations. In fact, manipulations of the type performed in section 3.2 show that these equations *do* have the form of equation (1*a*) but do not satisfy equation (1*b*). See [40] for a similar analysis of related works.

[2] In [20] there is an argument for the preservation of positivity for a damped harmonic oscillator. We believe that this argument is correct for infinitesimal times, but is not sufficient to prove positivity on timescales of order the memory time or longer. In [26] there is a general argument for the preservation of positivity, however we believe that this argument is only correct at infinite times. This reference also has an interesting discussion of conditions for positivity of a two-level system modelled (phenomenologically) by a Bloch equation with time-dependent parameters. However,

numerical studies (they evolved a finite number of initial conditions and checked that negative probabilities did not emerge). In contrast, for our model, we consider all *possible* initial conditions and thereby prove analytically that positivity is preserved.

It has been noted that course-graining can ensure positivity [27]. The work presented here indicates that the usual assumption of time-*independent* parameters in the master equation only leads to a violation of positivity for $t \lesssim t_{\mathrm{m}}$. Thus course-graining on such a scale could hide such a violation. It is also common to simplify Bloch–Redfield equations by making a rotating-wave approximation [14, 15, 28] which is also a form of course-graining since it 'averages out' fast oscillations. However if we treat the time dependence of the parameters correctly, the Bloch–Redfield equation is derived without any approximations which fail on short timescales, so it should preserve positivity without any course-graining.

There has been a lot of interest in a particular class of non-Markovian master equations which are positive by construction. They are either constructed by averaging Markovian master equations [29] or by measurement processes [30]. However, while these models are extremely interesting, we are not aware of works relating them to microscopic models of a typical qubit experiencing dissipation [31].

Finally, we mention that some works suggested that the reason for negative probabilities was the choice of factorized initial conditions [28, 32]. They argued that this initial condition was *unphysical*, and a more physical initial condition would not generate negative probabilities. However, factorized initial conditions correspond to any situation in which one makes a projective measurement of the system state at the start of the evolution. Thus, while other initial conditions are worthy of study [33, 34] (and highly relevant to certain experimental protocols), a factorized initial condition is *not* unphysical, and thus should not be able to generate negative probabilities. In this work, we restrict ourselves to factorized initial conditions (see section 3).

2. The Lindblad master equation

The Lindblad master equation, equations (1*a*) and (1*b*), is written in terms of a set of N^2 *trace-class* operators, $\{\hat{L}_n\}$ (where N is the number of levels of the system). Operators are trace-class if they form a complete orthonormal basis in the space of system operators, with the scalar product defined as $\left(\hat{L}_i^\dagger \cdot \hat{L}_j\right) \equiv \mathrm{tr}\left[\hat{L}_i^\dagger \hat{L}_j\right]$.[3] The basis is complete if any system operator can be written as $\hat{O}_{\mathrm{sys}} = \sum_j \hat{L}_j \,\mathrm{tr}\left[\hat{L}_j^\dagger \hat{O}_{\mathrm{sys}}\right]$. We choose L_0 to be proportional to the unit matrix. One can see that equation (1*a*) preserves the hermiticity and trace of the system's density matrix (the latter requires cyclic permutations inside the trace). The combination of equation (1*b*) with equation (1*a*) guarantees positivity. In fact it guarantees a stronger condition called *complete positivity*, which is the requirement that all probabilities remain positive even if the system became entangled with a second system at $t < 0$, but then does not interact with it again. For a review see sections 2.4 and 3 of [2], section VB of [15] or the introduction of [34]. In this paper we concern ourselves with studying positivity not complete positivity, however it has recently been shown [6] that the two are equivalent for the model that we study in section 6.

in our experience, master equations with negative coupling constants do not take the form of Bloch equations (see the model in section 6).

[3] As an example of a set of trace-class operators, consider a two-level system. One of many such sets of trace-class operators could be the following four operators $\hat{L}_0 = \hat{\sigma}_0/\sqrt{2}$, $\hat{L}_1 = \hat{\sigma}_x/\sqrt{2}$, $\hat{L}_2 = \hat{\sigma}_y/\sqrt{2}$ and $\hat{L}_3 = \hat{\sigma}_z/\sqrt{2}$, where $\sqrt{2}$ is for normalization. Yet there is nothing unique in this choice, and there is *no* requirement for hermiticity, so another possible choice could have $\hat{L}_1 = \hat{\sigma}_+$ and $\hat{L}_2 = \hat{\sigma}_-$, with $\hat{L}_0$ and $\hat{L}_z$ still as above. In any dissipative system the relevant basis of trace-class operators is given by the coupling to the environment.

Lindblad proved that equations (1*a*) and (1*b*) give the most general dynamical semigroup evolution [7, 8]. However to understand if this is applicable to a given system, one must ask if that system has the properties of a *dynamical semigroup*. For this one looks at the density-matrix propagator $\mathbb{K}(t;t_0)$, which acts on the density matrix at t_0 to give the density matrix at time t, so in terms of matrix elements

$$\hat{\rho}_{i'j'}(t) = \sum_{ij} \mathbb{K}_{i'j';ij}(t;t_0)\hat{\rho}_{ij}(t_0). \tag{2}$$

This super-operator, $\mathbb{K}(t;t_0)$, is an $N \times N \times N \times N$ tensor which acts on the $N \times N$ density matrix. Substituting it into equation (1*a*) gives a master equation for $\mathbb{K}_{i'j';ij}(t)$. The requirements for $\mathbb{K}(t;t_0)$ to form a dynamical semigroup are given in [2, 8, 15], they include (i) and (ii) and complete positivity. However another crucial requirement is that the propagator must be translationally invariant in time, so $\mathbb{K}(t;t_0) = \mathbb{K}(t-t_0)$ for all $t, t_0 > 0$ (where the system and environment were in a factorized state at time $t = 0$). Only then does $\mathbb{K}_{i''j'';ij}(t_2+t_1) = \sum_{i'j'} \mathbb{K}_{i''j'';i'j'}(t_2)\mathbb{K}_{i'j';ij}(t_1)$. Thus, a master equation must have *time-independent* parameters to have this semigroup property. If either the system Hamiltonian or the environment couplings (coupling constants λ_n or operators $\hat{L}_n$) are time dependent, then $\mathbb{K}(t;t_0)$ is *not* translationally invariant in time. Thus Lindblad's proof is inapplicable for such systems, even if their evolution is *Markovian* (in the sense that $\mathrm{d}\hat{\rho}(t)/\mathrm{d}t$ is a function only of $\hat{\rho}(t)$ not $\hat{\rho}(t' < t)$). So if λ_n or $\hat{L}_n$ are time dependent (as in our perturbative analysis) one cannot *a priori* state that negative λ_n will lead to a violation of positivity.

3. The perturbative (Bloch–Redfield) master equation

We assume that the system and environment start (at $t = 0$) in a factorized state $\hat{\rho}(t=0)\otimes\hat{\rho}_{\mathrm{env}}$. This would be the case if the experiment started with a perfect projective measurement of the state of the system[4]. The 'universe' (system + environment) then evolves under the Hamiltonian

$$\hat{\mathcal{H}}_{\mathrm{univ}} = \hat{\mathcal{H}}_{\mathrm{sys}} + \hat{\mathcal{H}}_{\mathrm{env}} + \hat{\Gamma}\hat{x}, \tag{3}$$

where $\hat{\Gamma}$ and $\hat{x}$ are system and environment operators, respectively. We treat these operators as Hermitian, because we assume they are observables (i.e. charge, magnetic dipoles, etc) as is the case in most qubit experiments (and more generally). Without lose of generality we can assume $\hat{\Gamma}$ is dimensionless and $\hat{x}$ has units of energy.

For a suitable environment one can derive the Bloch–Redfield master equation for the evolution of the system's reduced density matrix, $\hat{\rho}(t)$, from the evolution of the universe's state (tracing out the environment at time t). The assumptions necessary to derive this master equation are discussed in appendix A. Broadly speaking one needs an environment with a broad (almost) continuous spectrum of excitations, then the memory kernel of the environment (defined in equation (4*c*)) decays on a timescale t_{m}. Typically the Bloch–Redfield master equation is valid when the memory time, t_{m}, is much less than timescales associated with dissipation (relaxation and decoherence), which go like $1/(|\hat{\Gamma}\hat{x}|^2 t_{\mathrm{m}})$ (we set $\hbar = 1$ throughout this paper). The Bloch–Redfield master equation can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\mathrm{i}[\mathcal{H}_{\mathrm{sys}}, \hat{\rho}(t)]_- - \hat{\Gamma}\hat{\Xi}\hat{\rho}(t) - \hat{\rho}(t)\hat{\Xi}^\dagger\hat{\Gamma} + \hat{\Xi}\hat{\rho}(t)\hat{\Gamma} + \hat{\Gamma}\hat{\rho}(t)\hat{\Xi}^\dagger, \tag{4a}$$

[4] Some authors claim that factorized states are only relevant to those extremely rare situations in which the system–environment coupling is switched on at $t = 0$ (i.e. no coupling for all $t < 0$). This is incorrect. Even with finite coupling for all t (including $t < 0$), a projective measurement on the system at $t = 0$ prepares a given system state (with the experimenter knowing with certainty what this state is). This forces the total density matrix to be $\hat{\rho}(t=0) \otimes \hat{\rho}_{\mathrm{env}}$, where $\hat{\rho}(t=0)$ is the given (pure) system state.

with Γ being the operator in equation (3) and

$$\hat{\Xi} = \int_0^t \mathrm{d}\tau \alpha(\tau) \exp[-\mathrm{i}\hat{\mathcal{H}}_{\mathrm{sys}}\tau]\hat{\Gamma} \exp[\mathrm{i}\hat{\mathcal{H}}_{\mathrm{sys}}\tau]. \tag{4b}$$

Unlike many derivations we do not assume that we can take the upper-bound on this integral to ∞. The function $\alpha(\tau)$ is the environment's memory kernel given by

$$\alpha(\tau) = \mathrm{tr}_{\mathrm{env}}[\hat{x} \exp[-\mathrm{i}\hat{\mathcal{H}}_{\mathrm{env}}\tau]\hat{x} \exp[\mathrm{i}\hat{\mathcal{H}}_{\mathrm{env}}\tau]\hat{\rho}_{\mathrm{env}}(t)]. \tag{4c}$$

Since $\alpha(\tau)$ is typically complex, $\hat{\Xi}$ is not usually Hermitian (unlike $\hat{\Gamma}$). We assume that $\alpha(\tau)$ is independent of t, then $\alpha(-\tau) = \alpha^*(\tau)$. This is true if the environment is large enough that it is unaffected by the system–environment coupling (during the experiment) *and* the initial environment state obeys $[\mathcal{H}_{\mathrm{env}}, \hat{\rho}_{\mathrm{env}}] = 0$. The latter is the case if the environment is in an eigenstate or a classical mixture of eigenstates (such as a thermal state). We assume that $\alpha(\tau)$ is a decaying function of τ and define the memory time, t_{m}, as the timescale of that decay. Then $\hat{\Xi}$ is t-dependent, because t appears in the upper-bound on the integral in equation (4*b*).

Equation (4*a*) looks Markovian, in the sense that the rate of change of $\hat{\rho}(t)$ depends only on the value of $\hat{\rho}(t)$ (not the value of $\hat{\rho}(t')$ for $t' < t$). Despite this memory effects are present in the memory kernel, $\alpha(\tau)$. As we see in appendix A, if $\alpha(\tau)$ is finite for a given τ it means the rate of change of $\hat{\rho}$ at time t is affected by $\hat{\rho}(t-\tau)$. This is the reason for the time dependence of $\hat{\Xi}$, which is zero at $t = 0$, and grows to saturate on a timescale of order the environment memory time, t_{m}.

By writing $\hat{\Gamma}\hat{\Xi}\hat{\rho} - \hat{\rho}\hat{\Xi}^\dagger\hat{\Gamma} = \frac{1}{2}\big[(\hat{\Gamma}\hat{\Xi} + \hat{\Xi}^\dagger\hat{\Gamma}), \hat{\rho}\big]_+ - \mathrm{i}\big[\frac{\mathrm{i}}{2}(\hat{\Gamma}\hat{\Xi} - \hat{\Xi}^\dagger\hat{\Gamma}), \hat{\rho}\big]_-$, where $[A, B]_\pm = AB \pm BA$ are the anti-commutator/commutator, equation (4*a*) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\mathrm{i}[\hat{\mathcal{H}}'_{\mathrm{sys}}, \hat{\rho}(t)]_- - \frac{1}{2}[(\hat{\Gamma}\hat{\Xi} + \hat{\Xi}^\dagger\hat{\Gamma}), \hat{\rho}(t)]_+ + \hat{\Xi}\hat{\rho}(t)\hat{\Gamma} + \hat{\Gamma}\hat{\rho}(t)\hat{\Xi}^\dagger, \tag{5}$$

where we define $\hat{\mathcal{H}}'_{\mathrm{sys}} \equiv \hat{\mathcal{H}}_{\mathrm{sys}} - \frac{1}{2}\mathrm{i}(\hat{\Gamma}\hat{\Xi} - \hat{\Xi}^\dagger\hat{\Gamma})$. Even when $\hat{\Xi} \neq \hat{\Xi}^\dagger$, both $(\hat{\Gamma}\hat{\Xi} + \hat{\Xi}^\dagger\hat{\Gamma})$ and $\mathrm{i}(\hat{\Gamma}\hat{\Xi} - \hat{\Xi}^\dagger\hat{\Gamma})$ are Hermitian. The fact that $\hat{\mathcal{H}}'_{\mathrm{sys}}$ is Hermitian means that we can interpret it as a renormalized system Hamiltonian.

It is very convenient to define the symmetrized and anti-symmetrized spectral function of the noise, $S(\omega)$ and $A(\omega)$ such that

$$\frac{1}{2}[\alpha(\tau) + \alpha(-\tau)] = \mathrm{Re}\,[\alpha(\tau)] = \int \frac{\mathrm{d}\omega}{2\pi} S(\omega) \exp[-\mathrm{i}\omega\tau], \tag{6a}$$

$$\frac{1}{2}[\alpha(\tau) - \alpha(-\tau)] = \mathrm{i}\,\mathrm{Im}\,[\alpha(\tau)] = \int \frac{\mathrm{d}\omega}{2\pi} A(\omega) \exp[-\mathrm{i}\omega\tau], \tag{6b}$$

remembering that we set $\hbar = 1$ throughout. One can extract the form of $S(\omega)$ and $A(\omega)$ from environment details (a bath of harmonic oscillators [35], a bath of spins [36], etc). For an environment in thermal equilibrium at temperature T [37], $S(\omega)$ and $A(\omega)$ are related via $A(\omega) = S(\omega)\tanh(\omega/2k_{\mathrm{B}}T)$.[5] For harmonic oscillators, $A(\omega) \propto J(\omega)$ and so $S(\omega) \propto J(\omega)\coth(\omega/2k_{\mathrm{B}}T)$, where $J(\omega)$ is the spectral density in [35].

3.1. Dephasing and Lamb shift when a rotating-wave approximation is reasonable

When the dynamics is dominated by the system Hamiltonian (off-diagonal matrix elements decay over many Larmor oscillations), then we can make a rotating-wave (or secular)

[5] This relationship between $S(\omega)$ and $A(\omega)$ can be shown as follows. At thermal equilibrium $\hat{\rho}_{\mathrm{env}} = \sum_n P_n|n\rangle\langle n|$ where $|n\rangle$ is an eigenstate of $\hat{\mathcal{H}}_{\mathrm{env}}$ and $P_n \propto \exp[-E_n/k_{\mathrm{B}}T]$. In this case $S(\omega)$ and $A(\omega)$ are $\propto \sum_{nm} P_n|x_{mn}|^2[\delta(E_m - E_n - \omega) \pm \delta(E_m - E_n + \omega)]$, where $+(-)$ is for $S(\omega)$ $(A(\omega))$. Using $\sum_n = \int \mathrm{d}E'\nu(E')$ and then writing energy as the average and difference of E_m and E_n, we find $S(\omega)$ and $A(\omega)$ are $\propto \mathrm{e}^{\omega/2k_{\mathrm{B}}T} \pm \mathrm{e}^{-\omega/2k_{\mathrm{B}}T}$.

approximation [38] of equation (5). We write $\hat{\rho}(t)$ in the eigenbasis $\mathcal{H}_{\rm sys}$ (so $\mathcal{H}_{{\rm sys};ij} = E_i\delta_{ij}$), then we can expect $\hat{\rho}^{\rm rot}_{ij}(t) = {\rm e}^{{\rm i}(E_i-E_j)t}\hat{\rho}_{{\rm sys};ij}(t)$ to be insensitive to all fast oscillating contributions to its dynamics. We neglect ('average out') contributions to $\left({\rm d}\hat{\rho}^{\rm rot}_{ij}/{\rm d}t\right)$ which come from $\hat{\rho}_{{\rm sys};i'j'}$ when $i' \neq i$ or $j' \neq j$, since these contributions oscillate fast, at a rate $(E_{i'} - E_{j'} - E_i + E_j)$.[6] Then $({\rm d}/{\rm d}t)\hat{\rho}^{\rm rot}_{ij} = \left[{\rm i}\Delta E(i,j) - T_2^{-1}(i,j)\right]\hat{\rho}^{\rm rot}_{ij}$. The dephasing rate, at which a superposition of states i and j decays to a classical mixture ($1/T_2$ for two-level systems), is

$$T_2^{-1}(i,j) \simeq {\rm Re}\left[\tfrac{1}{2}(\hat{\Gamma}\hat{\Xi} + \hat{\Xi}^\dagger\hat{\Gamma})_{ii} + \tfrac{1}{2}(\hat{\Gamma}\hat{\Xi} + \hat{\Xi}^\dagger\hat{\Gamma})_{jj} - \hat{\Xi}_{ii}\hat{\Gamma}_{jj} - \hat{\Gamma}_{ii}\hat{\Xi}^\dagger_{jj}\right]. \tag{7}$$

The coupling to the environment also causes a Lamb shift; the precession rate is modified by the sum of the modification in $\hat{\mathcal{H}}'_{\rm sys}$ and $\Delta E(i,j)$, where $\Delta E(i,j)$ is the imaginary part of the square brackets in equation (7).

3.2. Writing the Bloch–Redfield equation as a Lindblad equation

To cast equation (5) in the Lindblad form, we rewrite it in terms of a set of orthonormal (trace-class) operators, $\{\hat{P}_i\}$. We use the usual Gram–Schmidt procedure; defining $\hat{P}_1 \propto \hat{\Gamma}$, and $\hat{P}_2$ as proportional to the component of $\hat{\Xi}$ which is orthogonal to $\hat{\Gamma}$. The constants of proportionality are such that both $\hat{P}_1$ and $\hat{P}_2$ are normalized. Hence

$$\hat{P}_1 = \frac{\hat{\Gamma}}{\sqrt{{\rm tr}[\hat{\Gamma}^2]}}, \qquad \hat{P}_2 = \frac{\hat{\Xi} - \hat{P}_1\,{\rm tr}[\hat{P}_1{}^\dagger\hat{\Xi}]}{\sqrt{{\rm tr}[\hat{\Xi}^\dagger\hat{\Xi}] - \left|\,{\rm tr}\left[\hat{P}_1{}^\dagger\hat{\Xi}\right]\right|^2}},$$

so $\hat{P}_1$ is Hermitian while in general $\hat{P}_2$ is not. As $\hat{P}_1$, $\hat{P}_2$ form an orthonormal basis, we have $\hat{\Gamma} = \hat{P}_1\,{\rm tr}[\hat{P}_1\hat{\Gamma}] + \hat{P}_2\,{\rm tr}[\hat{P}_2\hat{\Gamma}]$ and $\hat{\Xi} = \hat{P}_1\,{\rm tr}[\hat{P}_1\hat{\Xi}] + \hat{P}_2\,{\rm tr}[\hat{P}_2\hat{\Xi}]$. Then the Bloch–Redfield equation becomes

$$\frac{\rm d}{{\rm d}t}\hat{\rho}(t) = -{\rm i}[\mathcal{H}'_{\rm sys}, \hat{\rho}(t)] - \frac{1}{2}\sum_{ij} h_{ij}\left(\hat{P}_i^\dagger\hat{P}_j\hat{\rho}(t) + \hat{\rho}(t)\hat{P}_i^\dagger\hat{P}_j - 2\hat{P}_j\hat{\rho}(t)\hat{P}_i^\dagger\right). \tag{9}$$

In general, $h_{ij} = {\rm tr}[\hat{\Gamma}^\dagger\hat{P}_i]\,{\rm tr}\left[\hat{P}_j{}^\dagger\hat{\Xi}\right] + {\rm tr}[\hat{\Xi}^\dagger\hat{P}_i]\,{\rm tr}\left[\hat{P}_j{}^\dagger\hat{\Gamma}\right]$. However here ${\rm tr}\left[\hat{P}_2^\dagger\hat{\Gamma}\right] = 0$, so h_{ij} is given by the ij th element of the matrix

$$\mathbf{h} = b_z\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} + \begin{pmatrix}b_z & b_+\\ b_+^* & -b_z\end{pmatrix}, \tag{10}$$

where for the compactness in what follows we have defined

$$b_+ = {\rm tr}[\hat{\Gamma}^\dagger\hat{P}_1]\,{\rm tr}\left[\hat{P}_2{}^\dagger\hat{\Xi}\right], \qquad b_z = {\rm Re}\left({\rm tr}[\hat{\Gamma}^\dagger\hat{P}_1]\,{\rm tr}\left[\hat{P}_1^\dagger\hat{\Xi}\right]\right), \tag{11}$$

we also define $b^2 = |b_+|^2 + b_z^2$. We retain † s on the symbols to make the structure clear, however $\hat{\Gamma}^\dagger = \hat{\Gamma}$ and $\hat{P}_1^\dagger = \hat{P}_1 \propto \hat{\Gamma}$. The eigenvalues, $\lambda_{1,2}$, and the $SU(2)$ rotation, $\mathcal{U}$, to the eigenbasis of $\mathbf{h}$ are

$$\lambda_{1,2} = b_z \pm b, \qquad \mathcal{U} = \frac{1}{\sqrt{2}}\begin{pmatrix}(1+b_z/b)^{1/2} & \dfrac{b_+}{\sqrt{b(b+b_z)}}\\ \dfrac{b_+^*}{\sqrt{b(b+b_z)}} & -(1+b_z/b)^{1/2}\end{pmatrix}. \tag{12}$$

[6] The rotating-wave approximation fails if the dephasing rate is faster than $(E_{i'} - E_{j'} - E_i + E_{j'})$ with $i' \neq i$ and $j' \neq j$. Thus it always fails if there are (i) degeneracies (i.e. $E_{i'} = E_i$) or (ii) two gaps of equal magnitude (i.e. $E_{i'} - E_{j'} = E_i - E_j$) [39].

Performing this rotation on equation (9), the Bloch–Redfield equation takes the form of the Lindblad equation, equation (1*a*), with $\hat{L}_i = \sum_{j=1,2} \mathcal{U}_{ij} \hat{P}_j$[7]. However in general λ_2 is negative [14, 15], so this does *not* satisfy Lindblad's requirement in equation (1*b*).

4. Perturbative master equation for an extremely short memory time

We assume here that the memory time, t_m, is much shorter than any timescale in $\mathcal{H}_\mathrm{sys}$, i.e. $t_\mathrm{m} \ll \Delta_\mathrm{sys}^{-1}$ where Δ_sys is the largest energy difference in the system's spectrum. We substitute $\hat{\Gamma}(-\tau) = \hat{\Gamma} - \mathrm{i}[\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_- \tau - \frac{1}{2}[\hat{\mathcal{H}}_\mathrm{sys}, [\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_-]_- \tau^2 + \mathcal{O}[(\Delta_\mathrm{sys}\tau)^3]$ into $\hat{\Xi}$. We expect that $\alpha(\tau)$ is always given by a dimensionless function of τ/t_m multiplied by t_m^{-2} (given that $\hbar = 1$). Then $\hat{\Xi}(t)$ (having units of energy) is

$$\hat{\Xi}(t) = f_0(t)\hat{\Gamma} - \mathrm{i}t_\mathrm{m} f_1(t)[\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_- \\ -\tfrac{1}{2}t_\mathrm{m}^2 f_2(t)[\hat{\mathcal{H}}_\mathrm{sys}, [\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_-]_- + \mathcal{O}\big[t_\mathrm{m}^{-1}(\Delta_\mathrm{sys}t_\mathrm{m})^3\big], \tag{13}$$

where $f_q(t) = \int_0^t \mathrm{d}\tau (\tau/t_\mathrm{m})^q \alpha(\tau)$. For all q, $f_q(t)$ goes like t_m^{-1} multiplied by a dimensionless function of t/t_m. Thus equation (13) is an expansion to second-order in powers of $\Delta_\mathrm{sys}t_\mathrm{m}$. Writing $f_q(t)$ in terms of $S(\omega)$ and $A(\omega)$ we have

$$f_q(t) = \frac{\mathrm{i}}{(\mathrm{i}t_\mathrm{m})^q} \int \frac{\mathrm{d}\omega}{2\pi} \big(S(\omega) + A(\omega)\big) \frac{\mathrm{d}^q}{\mathrm{d}\omega^q} \left[\frac{1 - \mathrm{e}^{\mathrm{i}\omega t}}{\omega + \mathrm{i}0^+}\right], \tag{14}$$

where a positive infinitesimal constant, 0^+, ensures the convergence for $t \to \infty$. Thus

$$\hat{\Xi}(t) = \big(f_0(t)\sqrt{\mathrm{tr}[\hat{\Gamma}^2]} - \tfrac{1}{2}t_\mathrm{m}^2 f_2(t) K\big)\hat{P}_1 + t_\mathrm{m} f_1(t)\sqrt{2\,\mathrm{tr}[\hat{\Gamma}\hat{\mathcal{H}}_\mathrm{sys}[\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_-]}\,\hat{P}_2. \tag{15}$$

The only $f_2(t)$-term that we keep is in the prefactor on $\hat{P}_1$, for compactness we define $K \equiv \mathrm{tr}[\hat{\Gamma}[\hat{\mathcal{H}}_\mathrm{sys}, [\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_-]_-]/\sqrt{\mathrm{tr}[\hat{\Gamma}^2]}$. This term gives a $\mathcal{O}\big[t_\mathrm{m}^2\big]$-term in the final result, while other such $f_2(t)$-terms give at worst an $\mathcal{O}[t_\mathrm{m}^3]$-term. From equation (11), we get

$$b_+ = t_\mathrm{m} f_1(t)\sqrt{2\,\mathrm{tr}[\hat{\Gamma}^2]\,\mathrm{tr}[\hat{\Gamma}\hat{\mathcal{H}}_\mathrm{sys}[\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_-]}, \tag{16a}$$

$$b_z = \mathrm{Re}\,[f_0(t)]\,\mathrm{tr}[\hat{\Gamma}^2] - \tfrac{1}{2}t_\mathrm{m}^2\,\mathrm{Re}\,[f_2(t)]K\sqrt{\mathrm{tr}[\hat{\Gamma}^2]}. \tag{16b}$$

Since $\mathrm{tr}[\hat{\Gamma}\hat{\mathcal{H}}_\mathrm{sys}[\hat{\mathcal{H}}_\mathrm{sys}, \hat{\Gamma}]_-] \lesssim \Delta_\mathrm{sys}^2\,\mathrm{tr}[\hat{\Gamma}^2]$, we have $|b_+| \sim (\Delta_\mathrm{sys}t_\mathrm{m})b_z$ where $\Delta_\mathrm{sys}t_\mathrm{m} \ll 1$. The terms that we dropped only give contributions of order $(\Delta_\mathrm{sys}t_\mathrm{m})^2 b_z$.

To zeroth order in t_m we recover Lindblad's result, equations (1*a*) and (1*b*), with only one non-zero coupling constant $\lambda_1 = 2\,\mathrm{Re}\,[f_0]\,\mathrm{tr}[\hat{\Gamma}^2] > 0$, associated with the operator $\hat{L}_1 = (\mathrm{tr}[\hat{\Gamma}^2])^{-1/2}\hat{\Gamma}$. However to first order in t_m, we have equation (1*a*) with two non-zero coupling constant λ_1 and λ_2; the latter of which is negative (even for infinitesimal t_m). We use this model to explore the contradiction between Bloch–Redfield and Lindblad.

4.1. An environment with a nearly white-noise spectrum

Here we consider an environment with a nearly white-noise spectrum of excitations (a very wide Lorentzian), at extremely high temperature, $k_\mathrm{B}T \gg \omega_\mathrm{m}$, so

$$S(\omega) = S_0 \frac{\omega_\mathrm{m}^2}{\omega_\mathrm{m}^2 + \omega^2}, \qquad A(\omega) = \frac{\omega_\mathrm{m} S_0}{2k_\mathrm{B}T} \frac{\omega_\mathrm{m}\omega}{\omega_\mathrm{m}^2 + \omega^2}, \tag{17}$$

[7] The effective Hamiltonian $\hat{\mathcal{H}}'_\mathrm{sys} = \hat{\mathcal{H}}_\mathrm{sys} - \frac{1}{2}\sum_{ij} \tilde{h}_{ij} \hat{P}_i^\dagger \hat{P}_j$ with $\tilde{h}_{ij} = \mathrm{i}\,\mathrm{tr}[\hat{\Gamma}^\dagger \hat{P}_i]\,\mathrm{tr}[\hat{P}_j{}^\dagger \hat{\Xi}] - \mathrm{i}\,\mathrm{tr}[\hat{\Xi}^\dagger \hat{P}_i]\,\mathrm{tr}[\hat{P}_j{}^\dagger \hat{\Gamma}]$. Hence $\hat{\mathcal{H}}'_\mathrm{sys} = \hat{\mathcal{H}}_\mathrm{sys} - \frac{1}{2}\sum_{ij} h'_{ij} \hat{L}_i^\dagger \hat{L}_j$ where $h'_{ij} = [\mathcal{U}\tilde{\mathbf{h}}\mathcal{U}^\dagger]_{ij}$.

where $A(\omega)$ is given by the result below, equation (6*b*). The high-energy cut-off, $\omega_{\rm m}$, plays the role of the inverse memory time, $t_{\rm m}^{-1}$, so for nearly white noise we need it to be much larger than the largest system energy scale, $\Delta_{\rm sys}$. Then equation (14) gives

$$f_0(t) = \tfrac{1}{2}S_0(1+\mathrm{i}(2k_{\rm B}Tt_{\rm m})^{-1})(1-\exp[-t/t_{\rm m}]), \tag{18a}$$

$$f_1(t) = \tfrac{1}{2}S_0(1+\mathrm{i}(2k_{\rm B}Tt_{\rm m})^{-1})(1-(1+t/t_{\rm m})\exp[-t/t_{\rm m}]), \tag{18b}$$

$$f_2(t) = S_0(1+\mathrm{i}(2k_{\rm B}Tt_{\rm m})^{-1})\big(1-(1+t/t_{\rm m}+(t/t_{\rm m})^2/2)\exp[-t/t_{\rm m}]\big), \tag{18c}$$

where we evaluated the ω-integrals using complex analysis (by pushing the contours into the upper-half plane, one finds that the results are due to the pole at $\omega = \mathrm{i}\omega_{\rm m}$). Both $f_0(t)$ and $f_1(t)$ go exponentially to their long-time limit ($t \gg t_{\rm m}$), with the rate given by the memory time, $t_{\rm m}$. When $t/t_{\rm m} \gg 1$ we have $f_1(t)/f_0(t) \simeq 1$, while when $t/t_{\rm m} \ll 1$ we have $f_1(t)/f_0(t) \simeq t/t_{\rm m}$. For such an environment, the Bloch–Redfield equation is valid for $S_0 t_{\rm m} \ll 1$, see appendix A.

5. Positivity as a constraint on a two-level system's purity

To ensure that there is no basis in which the density matrix has negative probabilities (i.e. no possible measurement will return an unphysical probability) it is sufficient and necessary that the density matrix's eigenvalues, $\{\Lambda_k\}$, satisfy $0 \leqslant \Lambda_k \leqslant 1$ for all k. To see this, consider an arbitrary basis which is related to the eigenbasis by the unitary transformation, $\mathcal{U}$. In this basis all probabilities are given by $\hat{\rho}_{ii} = \sum_k |\hat{\mathcal{U}}_{ik}|^2 \Lambda_k$, where the unitarity of $\hat{\mathcal{U}}$ guarentees that $\sum_k |\hat{\mathcal{U}}_{ik}|^2 = 1$. Thus if $0 \leqslant \Lambda_k \leqslant 1$ for all k, then probabilities in this arbitrary basis satisfy $0 \leqslant \hat{\rho}_{ii} \leqslant 1$ for all i.

A two-level system is special because the eigenvalues of its density matrix are defined by a single parameter, s (remember that the sum of the eigenvalues must be one). The most general two-by-two density matrix is of the form $\hat{\rho} = \frac{1}{2}(\hat{\sigma}_0 + s_x\hat{\sigma}_x + s_y\hat{\sigma}_y + s_z\hat{\sigma}_z)$, where $\hat{\sigma}_{x,y,z}$ are the Pauli matrices, and $s_{x,y,z}$ are real numbers, when diagonalized it takes the form $\hat{\rho}_{\rm d} = \frac{1}{2}(\hat{\sigma}_0 + s\hat{\sigma}_z)$ with the single parameter $s^2 = s_x^2 + s_y^2 + s_z^2$. Thus to ensure positivity we require that $-1 \leqslant s \leqslant 1$. The purity of $\hat{\rho}$ is $P = \mathrm{tr}[\hat{\rho}^2] = \frac{1}{2}\big(1 + s_x^2 + s_y^2 + s_z^2\big)$, thus ensuring positivity is equivalent to ensuring that $P \leqslant 1$. This is not the case for systems with more than two levels[8].

Finally, it is worth noting that equation (1*a*) leads to

$$\frac{\mathrm{d}P}{\mathrm{d}t} = 2\,\mathrm{tr}\left[\hat{\rho}(t)\frac{\mathrm{d}\hat{\rho}(t)}{\mathrm{d}t}\right] = -2\sum_{n=0}^{N^2-1}\lambda_n\,\mathrm{tr}\big[\hat{L}_n^\dagger[\hat{L}_n,\hat{\rho}(t)]_-\hat{\rho}(t)\big]. \tag{19}$$

6. Two-level system with nearly white noise: proving positivity

We now consider a two-level system with $\mathcal{H}_{\rm sys} = -\frac{1}{2}B\hat{\sigma}_z$, coupled to an environment via $\hat{\Gamma} = \hat{\sigma}_x$. Then equation (4*b*) gives $\hat{\Xi} = \int_0^t \mathrm{d}\tau\alpha(\tau)[\hat{\sigma}_x\cos B\tau - \hat{\sigma}_y\sin B\tau]$, so $\hat{P}_1 = \hat{\sigma}_x/\sqrt{2}$ and $\hat{P}_2 = \hat{\sigma}_y/\sqrt{2}$. For an environment with a short memory time, equations (16*a*) and (16*b*) give $b_+ = 2Bt_{\rm m}f_1(t)$ and $b_z = 2\mathrm{Re}\,[f_0(t)] - (Bt_{\rm m})^2\,\mathrm{Re}\,[f_2(t)]$. Thus to second order in $Bt_{\rm m}$,

[8] Consider a three-level system whose density matrix is diagonal with the three following elements: $\rho_{11} = (1+x)/3$, $\rho_{22} = (1-x)/3$, $\rho_{33} = 1/3$. For $1 < x \leqslant \sqrt{3}$, this density matrix is unphysical because it is not positive (the probability $\rho_{22} < 0$), yet the purity $P \leqslant 1$.

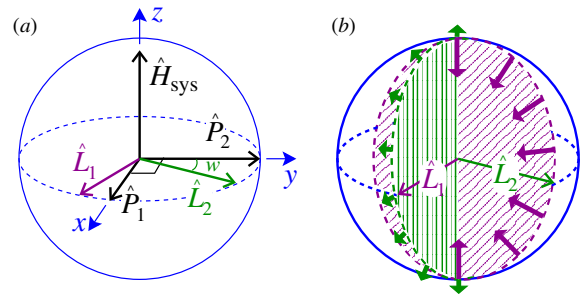

Figure 2. A sketch of the Bloch sphere, for the situation discussed in section 6. In (a), we show the axes associated with $\hat{\mathcal{H}}_{\rm sys}$, $\hat{P}_{1,2}$ and $\hat{L}_{1,2}$. We show $\hat{L}_{1,2}$ for a case where they are Hermitian (w is real), as only Hermitian operators are associated with axes in the Bloch sphere. In (b), we sketch the effect of the $\hat{L}_{1,2}$-terms on the evolution of the Bloch vector which represents the density matrix, $\mathbf{r}_{\rm Bloch} = (2{\rm Re}\,[\rho_{12}], -2{\rm Im}[\rho_{12}], \rho_{11} - \rho_{22})$. The $\hat{L}_1$-term *reduces* the magnitude of the vector in the plane perpendicular to $\hat{L}_1$ (diagonal cross-hatching) at a rate given by λ_1. The $\hat{L}_2$-term *increases* the magnitude of the vector in the plane perpendicular to $\hat{L}_2$ (vertical cross-hatching) at a rate given by $|\lambda_2| \ll |\lambda_1|$.

equation (12) gives

$$\begin{aligned}\lambda_1 &= 4\,{\rm Re}[f_0(t)] + (Bt_{\rm m})^2\left(\frac{|f_1(t)|^2}{{\rm Re}[f_0(t)]} - 2{\rm Re}[f_2(t)]\right)\\ \lambda_2 &= -\frac{(Bt_{\rm m})^2|f_1(t)|^2}{{\rm Re}\,[f_0(t)]}.\end{aligned} \tag{20}$$

Defining $w = Bt_{\rm m} f_1(t)/{\rm Re}\,[f_0(t)]$, the Lindblad operators, $\hat{L}_{1,2}$, are given by

$$\begin{pmatrix}\hat{L}_1\\ \hat{L}_2\end{pmatrix} = \mathcal{U}\begin{pmatrix}\hat{P}_1\\ \hat{P}_2\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1-\frac{1}{8}|w|^2 & w\\ w^* & -1+\frac{1}{8}|w|^2\end{pmatrix}\begin{pmatrix}\hat{\sigma}_x\\ \hat{\sigma}_y\end{pmatrix}. \tag{21}$$

Here we give $\mathcal{U}$ to first order in $Bt_{\rm m}$, but keep the higher-order terms necessary to ensure $\mathcal{U}^\dagger\mathcal{U} = 1$. Note that $\hat{L}_1$ and $\hat{L}_2$ are not Hermitian unless $f_1(t)$ is real.

We take the $T \to \infty$ limit of the nearly white noise in section 4.1 so ${\rm Im}[f_1(t)] = 0$, then w is real and gives the angle marked in figure 2(*a*). Defining the x'-, y'-axes such that $\hat{L}_1 = \hat{\sigma}_{x'}/\sqrt{2}$ and $\hat{L}_2 = \hat{\sigma}_{y'}/\sqrt{2}$, the Bloch–Redfield equation reduces to

$$\frac{{\rm d}}{{\rm d}t}\hat{\rho}(t) = -{\rm i}[\hat{\mathcal{H}}'_{\rm sys}, \hat{\rho}(t)] - 2\lambda_1(\hat{\rho}(t) - \hat{\sigma}_{x'}\hat{\rho}(t)\hat{\sigma}_{x'}) - 2\lambda_2(\hat{\rho}(t) - \hat{\sigma}_{y'}\hat{\rho}(t)\hat{\sigma}_{y'}). \tag{22}$$

The coupling constants, λ_1, λ_2, are given by equations (18*a*), (18*b*) and (20) with $T \to \infty$, so

$$\begin{aligned}\lambda_1 &= 2S_0(1 - {\rm e}^{-t/t_{\rm m}}) + \mathcal{O}[(Bt_{\rm m})^2],\\ \lambda_2 &= -(Bt_{\rm m})^2 S_0\frac{(1-(1+t/t_{\rm m})\,{\rm e}^{-t/t_{\rm m}})^2}{2(1-{\rm e}^{-t/t_{\rm m}})}.\end{aligned} \tag{23}$$

Substituting these results into equation (19), and writing $-\lambda_2$ as $+|\lambda_2|$ to emphasis that it tends to increase the purity, we get

$$\frac{{\rm d}P}{{\rm d}t} = -\lambda_1\,{\rm tr}[\hat{\rho}^2(t) - (\hat{\sigma}_{x'}\hat{\rho}(t))^2] + |\lambda_2|\,{\rm tr}[\hat{\rho}^2(t) - (\hat{\sigma}_{y'}\hat{\rho}(t))^2]. \tag{24}$$

6.1. Positivity at short times (times of order the memory time)

For times, t, much less than S_0^{-1} we can get the purity to first order in S_0, by integrating equation (24) with $\hat{\rho}(t)$ replaced by its value to zeroth order in S_0

$$\hat{\rho}^{(0)}(t) = \tfrac{1}{2}[1 + (s_x \cos Bt + s_y \sin Bt)\hat{\sigma}_{x'} + (s_y \cos Bt - s_x \sin Bt)\hat{\sigma}_{y'} + s_z\hat{\sigma}_z], \tag{25}$$

where the constants (s_x, s_y, s_z) define $\hat{\rho}(t = 0)$. Note that we have used the fact that $\hat{\mathcal{H}}'_{\rm sys} = \hat{\mathcal{H}}_{\rm sys} = -\beta\hat{\sigma}_z/2$ at zeroth order in S_0. Then equation (24) becomes

$$\frac{{\rm d}P(t)}{{\rm d}t} = -\lambda_1\big[(s_y \cos Bt - s_x \sin Bt)^2 + s_z^2\big] + |\lambda_2|\big[(s_x \cos Bt + s_y \sin Bt)^2 + s_z^2\big] + \mathcal{O}\big[S_0^2 t\big]. \tag{26}$$

As $t_{\rm m} \ll B^{-1}$, we can restrict ourselves to times $t \ll B^{-1}, S_0^{-1}$ (and hence expand in powers of Bt and $S_0 t$) and still study the dynamics up to times $\gg t_{\rm m}$. The problematic coupling constant, λ_2, is $\mathcal{O}[B^2]$, so we must expand the right-hand side of equation (26) to $\mathcal{O}[B^2]$, to see the effect of λ_2 on the dynamics. After this expansion in B, we expand the purity about $P(0) = 1$. So $P(t) = 1 + \int_0^t {\rm d}t'({\rm d}P(t')/{\rm d}t')$ gives

$$P(t) = 1 - 2S_0 t_{\rm m}\big[s_z^2 I_z + s_y^2 I_y - 2s_x s_y Bt_{\rm m} I_{xy} + s_x^2 (Bt_{\rm m})^2 I_x\big] + \mathcal{O}\big[S_0^2 t,\, S_0 B^3 t^3\big] \tag{27}$$

where I_z, I_y, I_{xy} and I_x are the following functions of $t/t_{\rm m}$:

$$I_z(t/t_{\rm m}) \equiv \int_0^t {\rm d}t' \frac{\lambda_1(t') + \lambda_2(t')}{2S_0 t_{\rm m}} \simeq \int_0^{t/t_{\rm m}} {\rm d}\nu(1 - {\rm e}^{-\nu}), \tag{28a}$$

$$I_y(t/t_{\rm m}) \equiv \int_0^t {\rm d}t' \frac{(1 - (Bt')^2)\lambda_1(t')}{2S_0 t_{\rm m}} \simeq \int_0^{t/t_{\rm m}} {\rm d}\nu(1 - {\rm e}^{-\nu}), \tag{28b}$$

$$I_{xy}(t/t_{\rm m}) \equiv \int_0^t {\rm d}t' \frac{t'\lambda_1(t')}{2S_0 t_{\rm m}^2} \simeq \int_0^{t/t_{\rm m}} {\rm d}\nu\nu(1 - {\rm e}^{-\nu}), \tag{28c}$$

$$I_x(t/t_{\rm m}) \equiv \int_0^t {\rm d}t' \frac{(Bt')^2\lambda_1(t') + \lambda_2(t')}{2S_0 B^2 t_{\rm m}^3} \simeq \int_0^{t/t_{\rm m}} {\rm d}\nu\left[\nu^2(1 - {\rm e}^{-\nu}) - \frac{[1 - (1+\nu)\,{\rm e}^{-\nu}]^2}{4(1 - {\rm e}^{-\nu})}\right], \tag{28d}$$

where $\nu = t'/t_{\rm m}$. The sign '$\simeq$' indicates that we keep only the leading order in $(Bt_{\rm m})$ in each term, this will be sufficient for our purposes.

To show that $P(t)$ does not exceed one (in the range of t for which equation (27) is valid), we show that the square bracket in equation (27) is never negative. Writing the square bracket as $\big[I_z s_z^2 + I_y(s_y - s_x(Bt_{\rm m})I_{xy}/I_y)^2 + s_x^2(Bt_{\rm m})^2\big(I_x - I_{xy}^2/I_y\big)\big]$, we see that there are three terms: the first two are always positive (but will be small for spins starting close to the x'-axis, i.e. $s_y, s_z \ll 1$), the third term is positive if $I_x > I_{xy}^2/I_y$. Thus we must show that $I_y I_x/I_{xy}^2 \geqslant 1$. For $t \ll t_{\rm m}$,

$$I_y \to \tfrac{1}{2}(t/t_{\rm m})^2 \qquad I_{xy} \to \tfrac{1}{3}(t/t_{\rm m})^3 \qquad I_x \to \tfrac{15}{64}(t/t_{\rm m})^4, \tag{29}$$

and for $t \gg t_{\rm m}$,

$$I_y \to t/t_{\rm m} \qquad I_{xy} \to \tfrac{1}{2}(t/t_{\rm m})^2 \qquad I_x \to \tfrac{1}{3}(t/t_{\rm m})^3. \tag{30}$$

Thus for $t \ll t_{\rm m}$ we have $I_y I_x/I_{xy}^2 \to 135/128$, while for $t \gg t_{\rm m}$ we have $I_y I_x/I_{xy}^2 \to 4/3$. For finite t we see that $I_y I_x/I_{xy}^2$ is a monotonic function of t which goes from $135/128$ to $4/3$ (see figure 3), thus it is always greater than 1. This means that $P(t) \leqslant 1$ for *all* times much less than S_0^{-1} (including times greater than $t_{\rm m}$).

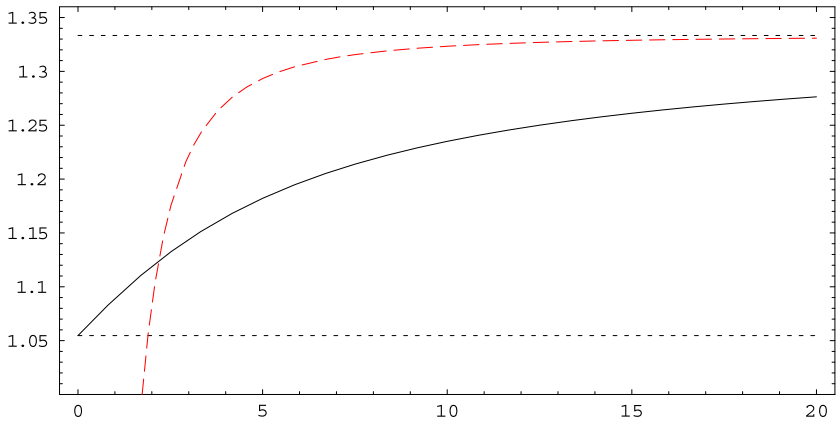

Figure 3. Plots of $I_y I_x / I_{xy}^2$ (solid curve) and $I_y^{(\infty)} I_x^{(\infty)} / (I_{xy}^{(\infty)})^2$ (dashed curve) as functions of $t/t_{\rm m}$. The two horizontal lines are the two extrema of $I_y I_x / I_{xy}^2$: its small t limit of 135/128 and its large t limit of 4/3. The crucial point is that $I_y I_x / I_{xy}^2 > 1$ for all $t \geqslant 0$. This is not the case for $I_y^{(\infty)} I_x^{(\infty)} / (I_{xy}^{(\infty)})^2$, which one would get if one mistakenly assumed time-independent coupling constants $\lambda_1(\infty)$, $\lambda_2(\infty)$; this is less than 1 for all $t/t_{\rm m} < \sqrt{3}$ and goes to $-\infty$ at $t = 0$.

For $t_{\rm m} \ll t \ll B^{-1}, S_0^{-1}$, the purity $P(t) = 1 - 2S_0 t\left[s_z^2 + \left(s_y - \frac{1}{2} s_x B t\right)^2 + \frac{1}{12}(s_x B t)^2\right]$. By checking all pure initial system states (state with $s_x^2 + s_y^2 + s_z^2 = 1$) we see that this is maximal for $s_x = \pm[1 + (Bt)^2/8] + \mathcal{O}[B^3 t^3]$, $s_y = \pm\frac{1}{2} Bt$ and $s_z = 0$ (where s_x and s_y have the same sign)[9]. Hence

$$P\left(t_{\rm m} \ll t \ll B^{-1}, S_0^{-1}\right) \leqslant 1 - \tfrac{1}{6} S_0 B^2 t^3. \tag{31}$$

This upper-bound on the purity will be crucial for our proof (in section 6.2) that the purity does not exceed one at longer times.

If we had made the usual assumption that one can replace $\lambda_1(t)$ and $\lambda_2(t)$ with $\lambda_1(t = \infty)$ and $\lambda_2(t = \infty)$ for all t, then we would have equations (28*a*)–(28*b*) with I_y, I_{xy}, I_x replaced by $I_y^{(\infty)} = \int_0^{t/t_{\rm m}} {\rm d}\nu$, $I_{xy}^{(\infty)} = \int_0^{t/t_{\rm m}} {\rm d}\nu\, \nu$ and $I_x^{(\infty)} = \int_0^{t/t_{\rm m}} {\rm d}\nu [\nu^2 - 1/4]$. We plot $I_y^{(\infty)} I_x^{(\infty)} \big/ \left(I_{xy}^{(\infty)}\right)^2$ in figure 3 and see that it goes to $-\infty$ as $t/t_{\rm m} \to 0$. Thus, such a mistaken assumption would have led us to conclude (as other have) that P can become bigger than 1 (at times $\lesssim t_{\rm m}$). The mistake is most clearly illustrated by looking at equation (27) with $s_x = 1$ and $s_y = s_z = 0$, then using $I_x^{(\infty)}$ in place of I_x would lead one to think that for $t \ll t_{\rm m}$ the purity would be $1 + \frac{1}{2} S_0 t$ when the correct expression shows it is $1 - \frac{2}{3} S_0 t_{\rm m} (t/t_{\rm m})^3$. Thus it is only by keeping the time dependence of the coupling constants, that we can show that the purity cannot exceed one for all times $\ll S_0^{-1}$ (including times greater than $t_{\rm m}$).

6.2. Positivity at long times (times of order and greater than S_0^{-1})

We now turn to the evolution of the purity at all times much greater than $t_{\rm m}$ (the long-time regime in figure 1). For times of order and greater than S_0^{-1} we need the full Bloch–Redfield equation, equation (22), not just the short time expansion of it. Since $t \gg t_{\rm m}$, the coupling

[9] This is easily shown by writing s_x, s_y, s_z in polar coordinates and showing that the maxima of the resulting function are at $(\theta, \phi) = (\pi/2, \frac{1}{2} Bt)$ and $(\theta, \phi) = (\pi/2, \pi + \frac{1}{2} Bt)$.

constants have saturated at their long time limits: $\lambda_1 = 2S_0$ and $\lambda_2 = -2S_0(Bt_m/2)^2$. Then equation (24) reduces to

$$\frac{dP(t)}{dt} = -2S_0\big[(1-(Bt_m/2)^2)s_z^2(t) + s_y^2(t) - (Bt_m/2)^2 s_x^2(t)\big]. \tag{32}$$

Since $Bt_m \ll 1$, we can see that $P(t \gg t_m)$ decays for nearly all $s_{x,y,z}(t)$. However the purity may grow if $s_y(t) \sim s_z(t) \sim \mathcal{O}[(Bt_m)^2]$; then the purity might exceed one (particularly if s_x is close to 1).

To see if the purity can exceed one, we expand the evolution about the time t_0, where we choose t_0 such that $s_y(t_0) = 0$. We then perform the same expansion about $t = t_0$ here as we performed about $t = 0$ in section 6.1. Hence on the right-hand side of equation (32) we make the substitution $s_x(t_0+\tau) = s'_x \cos B\tau$, $s_y(t_0+\tau) = s'_x \sin B\tau$, $s_z(t_0+\tau) = s'_z$, where we define $s'_x = s_x(t_0)$ and $s'_z = s_z(t_0)$ (remember that t_0 is chosen such that $s_y(t_0) = 0$). This substitution is good for all $\tau \ll S_0^{-1}$. After the substitution we expand the right-hand side of equation (32) up to second order in $B\tau$. Thus for $\tau \ll B^{-1}, S_0^{-1}$,

$$\left.\frac{dP(t)}{dt}\right|_{t=t_0+\tau} = -2S_0\big[(1-(Bt_m/2)^2)s_z'^2 + (s'_x B\tau)^2 - (s'_x Bt_m/2)^2\big]. \tag{33}$$

From this we see that the purity can only increase during a time window where $|\tau| < [(t_m/2)^2 - (s'_z/s'_x B)^2]^{1/2}$ (neglecting a term that is higher order in Bt_m). The maximum possible time for this growth is t_m (i.e. when $s'_z = 0$, P grows during the time window from $\tau = -\frac{1}{2}t_m$ to $\tau = \frac{1}{2}t_m$). Thus the assumption that $\tau \ll B^{-1}, S_0^{-1}$ is fulfilled for all τ at which the purity is growing.

At this point it is sufficient to make a gross overestimate of the amount by which the purity can grow. If we assumed that the purity grows during the entire time window $-\frac{1}{2}t_m \leqslant \tau \leqslant \frac{1}{2}t_m$ at the maximal possible rate (i.e. the rate at $\tau = 0$ when $s'_z = 0$ and $s_x = 1$), then during this time window it would grow by $\frac{1}{2}S_0B^2t_m^3$. If we define ΔP as the true increase of the purity in the time window where it grows, the overestimate enables us to put the following upper-bound:

$$\Delta P < \tfrac{1}{2}S_0B^2t_m^3. \tag{34}$$

Comparing this with the upper-bound on the purity in equation (31) with $t \gg t_m$ (but $t \ll S_0^{-1}$), we see that increasing the purity by ΔP cannot cause it to exceed one. The short- and long-time regimes overlap (see figure 1), so by showing that $P \leqslant 1$ in both regimes we have shown positivity for all $t > 0$.

7. Conclusions

The Bloch–Redfield master equation for an arbitrary system can be written in the form of a Lindblad master equation, equation (1*a*). Only by setting the memory time equal to zero (strictly Markovian evolution) do we recover Lindblad's result with coupling constants, $\{\lambda_n\}$, which are time independent and positive, equation (1*b*).

For finite memory times, the Bloch–Redfield master equation can still be cast in the form of equation (1*a*), but it does not satisfy equation (1*b*). However, the parameters are time dependent which means that the semigroup property is absent, and so Lindblad's requirements are *inapplicable*. We show analytically for a particular model (a two-level system coupled to a high-temperature environment with a memory time much less than system timescales) that the master equation preserves *positivity* if and only if we keep the time dependence of the parameters. Further, it turns out that *positivity* and *complete positivity* are equivalent for this particular model [6].

It is remarkable that our result only coincides with Lindblad's for strictly zero memory time, $t_m = 0$. If we take the limit $t_m \to 0$, we find that one coupling constant tends to zero from *below*. Further, we argue (see the appendix) that the Bloch–Redfield equations become exact in this limit. Thus even for infinitesimal t_m, one coupling constant is negative. Positivity (and hence complete positivity) is nonetheless preserved by the time dependence of the coupling constants at times of order the infinitesimal time t_m.

We wonder if an analysis of the time-dependent parameters of an arbitrary Bloch–Redfield master equation would show positivity or even complete positivity. If this could be proven, one could argue that the Bloch–Redfield master equation contains both the Lindblad equation and finite memory-time corrections to it.

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Appendix A. Deriving Bloch–Redfield from a Dyson equation

For completeness, we sketch the derivation of the Bloch–Redfield master equation [9, 10], using a common 'modern' approach [37] based on a real-time Dyson equation [13]. The derivation is nonetheless equivalent to [9, 10]. At $t = 0$ the system and environment are in a factorized state (e.g. a perfect projective measurement is made on the system at $t = 0$). The propagator of the system's reduced density matrix is $\mathbb{K}_{i'j';ij}(t;0) = \mathrm{tr}_{\mathrm{env}}[\langle i'|e^{-i\hat{\mathcal{H}}_{\mathrm{univ}}t}|i\rangle\hat{\rho}_{\mathrm{env}}\langle j|e^{i\hat{\mathcal{H}}_{\mathrm{univ}}t}|j'\rangle]$, with equation (2) giving the system's reduced density matrix at time t. The Dyson equation for $\mathbb{K}(t;t_0)$ (treating the system–environment interaction as a perturbation, which we keep to all orders) is

$$\mathbb{K}(t;0) = \mathbb{K}^{\mathrm{sys}}(t;0) + \int_0^t \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_1 \mathbb{K}^{\mathrm{sys}}(t;t_2)\boldsymbol{\Sigma}(t_2;t_1)\mathbb{K}^{\mathrm{sys}}(t_1;0), \tag{A.1}$$

where $\mathbb{K}(t;t')$ is the propagator including all interactions, $\mathbb{K}^{\mathrm{sys}}(t;t')$ is the bare system propagator (propagating it only under the Hamiltonian $\hat{\mathcal{H}}_{\mathrm{sys}}$). Since there are no interactions after $t = 0$ in the first term and after time t_2 in the second term above, we can trace out the environment at these times. Finally $\boldsymbol{\Sigma}(t_2;t_1)$ is an *irreducible* block of the propagator (with the same tensor structure as $\mathbb{K}(t;0)$), it is the smallest block for which the system has interacted with one or more environment excitations.

Taking the time derivative of equation (A.1) and noting that $(\mathrm{d}/\mathrm{d}t)\int_0^t \mathrm{d}t_2 \mathbb{K}^{\mathrm{sys}}(t;t_2)\mathbb{F}(t_2) = \mathbb{F}(t) + \int_0^t \mathrm{d}t_2 \mathbb{E}^{\mathrm{sys}}(t)\mathbb{K}^{\mathrm{sys}}(t;t_2)\mathbb{F}(t_2)$ for any $\mathbb{F}(t_2)$, we get the master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{K}(t;0) = -i\mathbb{E}^{\mathrm{sys}}(t)\mathbb{K}(t;0) + \int_0^t \mathrm{d}t_1 \boldsymbol{\Sigma}(t;t_1)\mathbb{K}(t_1;0). \tag{A.2}$$

We have defined $\mathbb{E}^{\mathrm{sys}}_{i'j';ij} = \langle i'|\mathcal{H}_{\mathrm{sys}}|i\rangle\langle j|\mathcal{H}_{\mathrm{sys}}|j'\rangle$, then $(\mathrm{d}/\mathrm{d}t)\mathbb{K}^{\mathrm{sys}}(t;0) = -i\mathbb{E}^{\mathrm{sys}}(t)\mathbb{K}^{\mathrm{sys}}(t;0)$. To clearly see the non-Markovian nature of equation (A.2) we can substitute it into equation (2) which gives $(\mathrm{d}/\mathrm{d}t)\hat{\rho}(t) = -i[\hat{\mathcal{H}}_{\mathrm{sys}}(t), \hat{\rho}(t)] + \int_0^t \mathrm{d}t_1 \boldsymbol{\Sigma}(t;t_1)\hat{\rho}(t_1)$. This master equation is exact, our only assumption was that the system and environment were in a factorized

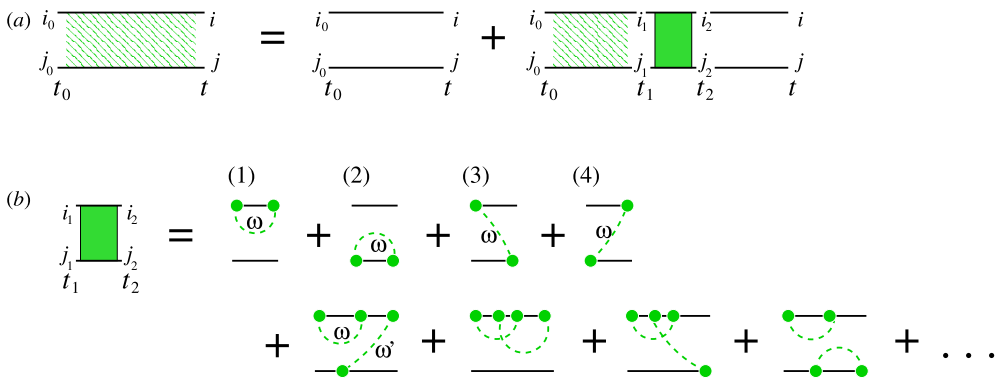

Figure A1. (a) Real time Dyson equation for an arbitrary system. The pair of lines with cross-hatching between them are the full propagator, $\mathbb{K}(t'';t')$; the lines without cross-hatching are the bare system propagator, $\mathbb{K}^{\rm sys}(t'';t')$; and the lines with solid colour between them are the irreducible block, $\mathbf{\Sigma}(t'',t')$. Internal indices are summed over and internal times are integrated over as in equation (A.1). This drawing of the propagators emphasizes that only $\mathbb{K}^{\rm sys}_{i'',j'';i'j'}(t'';t')$ can be written in the form $A_{i'';i'} \times B_{j'';j'}$. (b) Some lower-order diagrams for the irreducible block, $\mathbf{\Sigma}(t'',t')$, in all cases we integrate ω, ω', etc, over the spectrum of excitations. The second-order diagrams are labelled (1)–(4).

state at time $t = 0$. It is formally equivalent to the Nakajima–Zwanzig equation [11, 12]. However it is of little practical use (giving no great advantage over standard perturbation theory) unless the irreducible block, $\mathbf{\Sigma}(t_2;t_1)$, is reasonably local in time, i.e. decays on a scale $t_2 - t_1 \ll t$. Without approximation we can use $\hat{\rho}(t) = \mathbb{K}(t;t_1)\hat{\rho}(t_1)$ to write this master equation as

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\mathrm{i}[\hat{\mathcal{H}}_{\rm sys}(t), \hat{\rho}(t)] + \int_0^t \mathrm{d}t_1 \mathbf{\Sigma}(t;t_1)\mathbb{K}^{-1}(t;t_1)\hat{\rho}(t). \tag{A.3}$$

This might 'look' Markovian, but the non-Markovian nature is in the new term $\mathbb{K}^{-1}(t;t_1)$. Approximations of equation (A.3) will give a Bloch–Redfield master equation.

A.1. The Bloch–Redfield equation from a Born approximation

Here we get the Bloch–Redfield master equation by making a Born approximation of the irreducible block $\mathbf{\Sigma}(t'',t')$ in equation (A.3). It involves neglecting all contributions to $\mathbf{\Sigma}(t'',t')$ beyond second order. Our derivation involves two assumptions which justify the Born approximation (other derivations may be possible).

Our first assumption is that the environment is large enough to have a continuous energy spectrum of excitations (although it does not matter if this spectrum is discrete on scales $\ll t^{-1}$). So for finite relaxation/decoherence rates, we assume the coupling to each environment excitation is small enough to be treated only up to second order. Thus each excitation evolves only under $\hat{\mathcal{H}}_{\rm env}$ up to the time of its (first or second order) interaction with the system. It then never interacts with the system again, so we trace it out immediately after the (first or second order) interaction.

Our second assumption is that the environment's initial density matrix obeys $[\hat{\mathcal{H}}_{\rm env}, \hat{\rho}_{\rm env}] = 0$, as would be the case for either an eigenstate or any classical mixture of eigenstates of $\hat{\mathcal{H}}_{\rm env}$ (such as a thermal state). Combining this with our first assumption means that we can treat $\hat{\rho}_{\rm env}$ as time independent. Then without loss of generality we can make $\mathrm{tr}_{\rm env}[\hat{x}\hat{\rho}_{\rm env}] = 0$, by moving any constant off-set into the definition of $\hat{\mathcal{H}}_{\rm sys}$. This removes

the first-order contributions from the irreducible block, $\mathbf{\Sigma}(t'', t')$. Thus $\mathbf{\Sigma}(t'', t')$ becomes the sum of second-order (and higher-order) terms sketched in figure A1(*b*). The dotted lines indicate that a given environment excitation (with energy ω) has been created by the system–environment interaction.

Treating the integral in equation (A.3) to lowest (second) order in $\hat{x}$, means making a Born approximation on $\mathbf{\Sigma}(t'', t')$ and treating $\mathbb{K}^{-1}(t; t_1)$ to zeroth order in $\hat{x}$[10]. Hence defining $\tau = t - t_1$ and $\mathbb{S}(\tau) = \mathbf{\Sigma}^{\text{Born}}(t; t-\tau)[\mathbb{K}^{\text{sys}}(t; t-\tau)]^{-1}$, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\mathrm{i}[\hat{\mathcal{H}}_{\text{sys}}(t), \hat{\rho}(t)] + \int_0^t \mathrm{d}\tau \mathbb{S}(\tau)\hat{\rho}(t). \tag{A.4}$$

The four contributions to $\mathbf{\Sigma}^{\text{Born}}(t; t-\tau)$, labelled (1)–(4) in figure A1(*b*), give

$$\mathbb{S}^{(1)}_{i'j';ij}(\tau) = \text{tr}_{\text{env}}[\langle i'|\hat{\Gamma}\hat{x}\,\mathrm{e}^{-\mathrm{i}\hat{\mathcal{H}}_0\tau}\hat{\Gamma}\hat{x}\,\mathrm{e}^{\mathrm{i}\hat{\mathcal{H}}_0\tau}|i\rangle\rho_{\text{env}}\langle j|j'\rangle], \tag{A.5a}$$

$$\mathbb{S}^{(2)}_{i'j';ij}(\tau) = \text{tr}_{\text{env}}[\langle i'|i\rangle\rho_{\text{env}}\langle j|\mathrm{e}^{-\mathrm{i}\hat{\mathcal{H}}_0\tau}\hat{\Gamma}\hat{x}\,\mathrm{e}^{\mathrm{i}\hat{\mathcal{H}}_0\tau}\hat{\Gamma}\hat{x}|j'\rangle], \tag{A.5b}$$

$$\mathbb{S}^{(3)}_{i'j';ij}(\tau) = \text{tr}_{\text{env}}[\langle i'|\mathrm{e}^{-\mathrm{i}\hat{\mathcal{H}}_0\tau}\hat{\Gamma}\hat{x}\,\mathrm{e}^{\mathrm{i}\hat{\mathcal{H}}_0\tau}|i\rangle\rho_{\text{env}}\langle j|\hat{\Gamma}\hat{x}|j'\rangle], \tag{A.5c}$$

$$\mathbb{S}^{(4)}_{i'j';ij}(\tau) = \text{tr}_{\text{env}}[\langle i'|\hat{\Gamma}\hat{x}|i\rangle\rho_{\text{env}}\langle j|\mathrm{e}^{\mathrm{i}\hat{\mathcal{H}}_0\tau}\hat{\Gamma}\hat{x}\,\mathrm{e}^{-\mathrm{i}\hat{\mathcal{H}}_0\tau}|j'\rangle], \tag{A.5d}$$

where we define $\hat{\mathcal{H}}_0 = \hat{\mathcal{H}}_{\text{sys}} + \hat{\mathcal{H}}_{\text{env}}$. We rewrite all these contributions in terms of operators acting to the left and right of the density matrix, $\hat{\rho}(t)$. Those interaction on the upper line are to the left of $\hat{\rho}(t)$, while those on the lower line are to the right. Thus summing these four terms we get

$$\begin{aligned}\mathbb{S}(\tau)\hat{\rho}(t) = \text{tr}_{\text{env}}[&\hat{\Gamma}(0)\hat{x}(0)\hat{\Gamma}(-\tau)\hat{x}(-\tau)[\hat{\rho}(t)\otimes\rho_{\text{env}}] + [\hat{\rho}(t)\otimes\rho_{\text{env}}]\hat{\Gamma}(-\tau)\hat{x}(-\tau)\hat{\Gamma}\hat{x}\\ &+\hat{\Gamma}(-\tau)\hat{x}(-\tau)[\hat{\rho}(t)\otimes\rho_{\text{env}}]\hat{\Gamma}(0)\hat{x}(0) + \hat{\Gamma}(0)\hat{x}(0)[\hat{\rho}(t)\otimes\rho_{\text{env}}]\hat{\Gamma}(-\tau)\hat{x}(-\tau)],\end{aligned}$$

where the operators are in the interaction picture, so

$$\hat{\Gamma}(\tau) = \exp[\mathrm{i}\hat{\mathcal{H}}_{\text{sys}}\tau]\hat{\Gamma}\exp[-\mathrm{i}\hat{\mathcal{H}}_{\text{sys}}\tau] \qquad \text{and} \qquad \hat{x}(\tau) = \exp[\mathrm{i}\hat{\mathcal{H}}_{\text{env}}\tau]\hat{x}\exp[-\mathrm{i}\hat{\mathcal{H}}_{\text{env}}\tau].$$

Substituting this into equation (A.4) we get the Bloch–Redfield master equation that we gave in section 3.

Finally, to see *when* the Born approximation is justified, we must estimate the higher-order contributions that we are neglecting. The higher-order contributions to $\mathbf{\Sigma}(t; t_1)$ take a similar form to the second-order ones, but have more factors of $\hat{\Gamma}\hat{x}$ acting to the left and right of the density matrix. The times at which these interactions can occur are chosen such that that $\mathbf{\Sigma}(t; t_1)$ is irreducible (as discussed above). A typical fourth-order contribution (those in the second line of figure A1(*b*)) will go like $|\hat{\Gamma}\hat{x}|^4 t_{\text{m}}^3$, compared with the second-order terms that went like $|\hat{\Gamma}\hat{x}|^2 t_{\text{m}}$. It is justifiable to neglect the fourth order while keeping the second order, only if $|\hat{\Gamma}\hat{x}|t_{\text{m}} \ll 1$. Physically the constraint that $|\hat{\Gamma}\hat{x}|t_{\text{m}} \ll 1$ means that the Bloch–Redfield master equation applies to situations where the decay rate of memory effects, t_{m}^{-1}, is much faster than dissipative (relaxation and decoherence) rates $\sim |\hat{\Gamma}\hat{x}|^2 t_{\text{m}}$. There is no constraint on the ratio of dissipative rates to the system's energy scales, so the Bloch–Redfield equation can be applicable to strong (over-damped) and weak (under-damped) dissipation.

[10] Since we approximate $\mathbb{K}$ by $\mathbb{K}^{\text{sys}}$, and not by 1, our derivation is equivalent to Redfield's [10], and *not* the summary of Redfield's derivation in [2].

Appendix B. A simple picture of initial slips

To understand how *initial slips* work [16–24], it is helpful to neglect the matrix structure of the master equation. One then has a trivial differential equation of the following form (F and ρ now being numbers not matrices):

$$(\mathrm{d}/\mathrm{d}t)\rho(t) = -F(t)\rho(t), \tag{B.1}$$

where $F(t)$ is time dependent, but saturates at a finite value, f_∞, for times greater than the memory time (F and ρ are now numbers, not matrices). This is traditionally approximated by [1, 2]

$$(\mathrm{d}/\mathrm{d}t)\rho(t) = -f_\infty\rho(t). \tag{B.2}$$

Equation (B.2) gives the wrong evolution for any initial condition, $\rho(0)$, because it is not justified for times less than the memory time. However, by multiplying $\rho(0)$ by an *initial slip* one can ensure that the evolution under the incorrect, equation (B.2), coincides with the evolution under the correct, equation (B.1), for all times much *greater* than the memory time. For the above equations the initial slip is simply $\exp\left[-\int_0^t \mathrm{d}t'[F(t') - f_\infty]\right]$. For t much greater than the memory time, t_m, the initial-slip becomes time-independent (one can take the integral's upper limit to infinity since $[F(t') - f_\infty] \sim 0$ for $t' \gg t_\mathrm{m}$). Then the initial slip becomes time independent. Thus one can take $\rho(0)$, 'slip it' so that it becomes $\exp\left[-\int_0^\infty \mathrm{d}t'[F(t') - f_\infty]\right]\rho(0)$, and use that as the initial condition for evolution under the incorrect, equation (B.2). The resulting $\rho(t)$ will coincide with the correct result for all times much greater than the memory time, but will be absolutely meaningless for all times of order the memory time. Qualitatively the same analysis applies to the full master equation, but it is complicated by the matrix structure of the master equation (see e.g. [23])

The above sketch of the initial-slip method makes it clear that it is *not* suited to our analysis of positivity. The short-time dynamics (on timescales of order the memory time) that it generates are *fictitious*, a sudden initial slip of the density matrix followed by evolution under an incorrect master equation. Studying the positivity for these fictitious short-time dynamics tells us nothing about whether the true short-time dynamics preserves positivity or not.

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