Correlation functions in finite memory-time reservoir theory

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Interaction of a small system S with a large reservoir R amounts to thermal relaxation of the reduced system density operator $\rho_S(t)$. The presence of the reservoir enters the equation of motion for $\rho_S(t)$ through the reservoir correlation functions $f_{kl}(\tau)$ (defined in the text), which decay to zero for $\tau\to\infty$ on a time scale τ_c. Commonly, this τ_c is much smaller than the inverse relaxation constants for the time evolution of $\rho_S(t)$. Then a series of approximations can be made, which lead to a Markovian equation of motion for $\rho_S(t)$. In this paper the assumption of a small reservoir correlation time is removed. The equation of motion for $\rho_S(t)$ is solved, and it appears that the memory effect, due to $\tau_c \not\simeq 0$, can be incorporated in a frequency dependence of the relaxation operator $\widetilde{\Gamma}(\omega)$. Subsequently, (unequal-time) quantum correlation functions of two system operators are considered, where explicit expressions for (the Laplace transform of) the correlation functions are obtained. They involve again the relaxation operator $\widetilde{\Gamma}(\omega)$, which accounts for the time regression. Additionally it is found that an initial-correlation operator $\widetilde{\Upsilon}(\omega)$ arises, as a consequence of the fact that the equal-time correlation functions do not factorize as $\rho_S(t)$ times the reservoir density operator. It is pointed out that the frequency dependence of $\widetilde{\Gamma}(\omega)$ and the occurrence of a nonzero $\widetilde{\Upsilon}(\omega)$ both arise as a result of $\tau_c \not\simeq 0$, and should therefore be treated on an equal footing. Explicit evaluation of $\widetilde{\Gamma}(\omega)$ and $\widetilde{\Upsilon}(\omega)$ shows that their matrix elements can be expressed entirely in $\tilde{f}_{kl}(\omega)$, just as in the Markov approximation. Hence no essential complications appear if one should go beyond the limits of a small reservoir correlation time τ_c.

I. INTRODUCTION

In many practical cases the equation for the evolution of the density operator $\rho(t)$ of a quantum system assumes the general form

$$i\hbar\frac{d}{dt}\rho(t) = [H'_S + H_R + H'_I,\rho(t)], \tag{1.1}$$

where H'_S and the H_R pertain to separated components S (= system) and R (= reservoir) of the entire configuration, and H'_I denotes an interaction between S and R. Probably the most familiar example is spontaneous decay of an excited atom in empty space. Then, H'_S equals the atomic Hamiltonian (internal structure), H_R represents the electromagnetic field, and H'_I is the dipole coupling between the atom and the electric component of the radiation field, which causes the spontaneous transitions. Since H_R has a large (infinite) number of eigenstates, an exact diagonalization of the complete Hamiltonian $H'_S + H_R + H'_I$ is intractable. The interest is, however, in the behavior of the atom, as it is determined by its interaction with the radiation field (vacuum or black-body radiation). Therefore, one introduces the reduced atomic (system) density operator by

$$\rho_S(t) = \mathrm{Tr}_R\,\rho(t), \tag{1.2}$$

where the trace runs over all states of the radiation field (the reservoir). The issue of reservoir, relaxation, or heat-bath theory is then to derive an accurate equation of motion for $\rho_S(t)$, in which the properties of R only enter as simple (and explicit) parameter functions. In the theory of spontaneous decay these are the Einstein coefficients and the Lamb shifts.

Most crucial for the development of a relaxation theory is the concept of a large reservoir. If the system S were not present, the reservoir would be in a (thermal equilibrium) state $\bar\rho_R$, which obeys

$$[H_R,\bar\rho_R] = 0,\quad \bar\rho_R^\dagger = \bar\rho_R,\quad \mathrm{Tr}_R\,\bar\rho_R = 1, \tag{1.3}$$

and it is assumed that the interaction between S and R does not substantially affect this reservoir state. Or more precisely, the state $\bar\rho_R$ changes a little due to the interaction with S, but the effect on the time evolution of the system density operator $\rho_S(t)$ is negligible. In the quoted example this implies that an atom in complete vacuum should decay in the same fashion as an atom in space with a single photon present. As a consequence of this large-reservoir assumption, we can factorize the density operator as

$$\rho(t) \simeq \rho_S(t)\bar\rho_R, \tag{1.4}$$

in places where the value of $\rho(t)$ determines the strength of the interaction.

In order to derive a relatively simple equation for $\rho_S(t)$, a sequence of additional approximations is usually made, which rely on the fact that the reservoir correlation time τ_c is short in comparison with the inverse relaxation constants $1/\Gamma$. The idea is as follows. One derives an equation for $\rho_S(t)$ which contains a quantity of the form $\langle R(t)R(0)\rangle$, with R a typical reservoir operator (for instance the electric field), and where the angular brackets indicate an average with the density operator $\bar\rho_R$, e.g.,

$$\langle\cdots\rangle = \mathrm{Tr}_R\,\bar\rho_R(\cdots)\,. \tag{1.5}$$

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Due to the many eigenvalues $\hbar\omega$ of H_R and the large cutoff frequency ω_c, the function $\langle R(t)R(0)\rangle$ will decay to zero on a time scale of the order of $\tau_c \sim 1/\omega_c$. On the other hand, as a result of the interaction between S and R, the system density operator $\rho_S(t)$ will decay on a time scale $1/\Gamma$ (with Γ an Einstein coefficient, for instance), and in many cases the relation

$$\Gamma\tau_c \ll 1 \tag{1.6}$$

holds. The validity of (1.6) allows a series of approximations (see the Appendix), commonly referred to as the Markov approximation.

For spontaneous decay the restriction (1.6) is rigorously justified, and the equation of motion for $\rho_S(t)$ is known for more than a decade.[1-3] However, not every reservoir has a short correlation time. For instance, an adsorbed atom or molecule on a surface interacts with the substrate through phonon coupling (crystals) or electron-hole pair creation (metals). In the case of physisorbed atoms on a harmonic crystal, the Hamiltonian H_S' accounts for the kinetic and potential energy of the atom. The potential supports bound states, separated by $\sim 10^6$–10^8 MHz (infrared), which is resonant with the thermal excitations of the crystal (phonons). Mechanical coupling (vibrations) between the adsorbed atom and the lattice atoms gives rise to thermal relaxation of the adbond system.[4-6] Typical relaxation constants acquire an order of magnitude of 10^3–10^6 MHz, whereas the cutoff frequency (Debye frequency) is of the order of 10^6 MHz. For electron-hole pair formation the situation is even worse, where we have $\Gamma\tau_c \gtrsim 1$ so that a Markov approximation can never be justified.[7]

There exist many relaxation theories. Most notable are the projection techniques,[8-10] a Langevin formulation,[2] and, as we adopt here, a reservoir approach.[11-13] A feature of the quoted theories is that they all lead to the same result as soon as the Markov approximation is imposed. Several attempts have been undertaken to drop this Markov assumption.[14-16] To the best of our knowledge, however, a treatment free of inconsistencies and leading to explicit expressions (rather than formal expressions which cannot be evaluated) was never formulated.

II. RESERVOIR INTEGRAL

In this section we set up the notation and derive an integral of Eq. (1.1), which is appropriate for imposing the reservoir assumption. The first step is a redefinition of the system Hamiltonian. We recall that the interaction Hamiltonian H_I' is an operator in $S+R$ space, and therefore its reservoir average $\langle H_I'\rangle$ will be an operator in S space. In order to eliminate so-called secular terms, we define the new system and interaction Hamiltonians by

$$H_S = H_S' + \langle H_I'\rangle\,, \tag{2.1}$$

$$H_I = H_I' - \langle H_I'\rangle\,, \tag{2.2}$$

and the advantage of this rearrangement comes from the fact that the reservoir average of H_I equals zero. Explicitly,

$$\langle H_I\rangle = 0. \tag{2.3}$$

A compact and transparent representation of reservoir theory can be obtained with a Liouville-operator formalism. If we introduce the Liouvillians L_α by

$$L_\alpha\sigma = \hbar^{-1}[H_\alpha,\sigma]\,, \quad \alpha = S,R,I, \tag{2.4}$$

which defines their action on an arbitrary operator σ in $S+R$ space, then the equation of motion (1.1) becomes

$$i\frac{d}{dt}\rho(t) = (L_S + L_R + L_I)\,\rho(t)\,. \tag{2.5}$$

For later purposes we mention a few properties of the Liouvillians. First, L_S and L_R commute, since they act on a different part of Liouville space. Second, L_R stands for a commutator, which implies the relation

$$\mathrm{Tr}_R\, L_R\sigma = 0, \tag{2.6}$$

for any σ. From $[H_R,\bar\rho_R] = 0$, Eq. (1.3), we find

$$e^{-iL_R t}\bar\rho_R = \bar\rho_R\,, \tag{2.7}$$

and due to the shift of the interaction over its average, L_I obeys

$$\mathrm{Tr}_R\, L_I(\sigma_S\bar\rho_R) = 0. \tag{2.8}$$

Here and in the following, σ_S will indicate an arbitrary operator in S space.

An integral of Eq. (2.5) reads

$$\rho(t) = e^{-i(L_S+L_R)(t-t_0)}\rho(t_0) - i\int_{t_0}^{t} dt'\, e^{-i(L_S+L_R)(t-t')}L_I\rho(t')\,, \tag{2.9}$$

and substitution into Eq. (2.5) then yields

$$i\frac{d}{dt}\rho(t) = (L_S + L_R)\rho(t) + L_I e^{-i(L_S+L_R)(t-t_0)}\rho(t_0) - iL_I\int_{t_0}^{t} dt'\, e^{-i(L_S+L_R)(t-t')}L_I\rho(t')\,, \tag{2.10}$$

which is an exact integral of the equation of motion. If we subsequently take the trace over the reservoir states, the left-hand side becomes $i\,d\rho_S(t)/dt$, which equals the rate of change of the system density operator due to the free evolution [the term $L_S\rho_S(t)$ on the right-hand side] and the coupling to the reservoir (terms proportional to L_I). Hence the integral in Eq. (2.10) accounts for the relaxation of $\rho_S(t)$, and its value is proportional to the coupling strength. Therefore we can adopt the reservoir assumption, Eq. (1.4), on $\rho(t')$ in the integrand. We then find the equation of motion for $\rho_S(t)$ to be

$$i\frac{d}{dt}\rho_S(t) = L_S\rho_S(t) + \mathrm{Tr}_R\, L_I e^{-i(L_S+L_R)(t-t_0)}\rho(t_0) - i\,\mathrm{Tr}_R\, L_I\int_{t_0}^{t} dt'\, e^{-i(L_S+L_R)(t-t')} \times L_I(\rho_S(t')\bar\rho_R)\,, \tag{2.11}$$

for $t \geqslant t_0$. It is important to note that the initial value $\rho(t_0)$ of the density operator (not the system part) remains present in the equation of motion for $\rho_S(t)$, in general. Equation (2.5) determines the time evolution of $\rho(t)$ for $t \geqslant t_0$, and the solution of Eq. (2.5) is fixed as soon as an initial value $\rho(t_0)$

is prescribed. Since $\rho(t_0)$ is not determined by the equation of motion, a further specification of the initial state $\rho(t_0)$ is necessary.

III. DENSITY OPERATOR

For finite memory-time reservoirs the choice of $\rho(t_0)$ is more than a matter of convenience. If the system has been in contact with the reservoir prior to t_0, then $\rho(t_0)$ is determined by its time evolution in the recent past $t<t_0$, and consequently the value of $\rho(t_0)$ is no longer arbitrary. As a solution, we simply define the instant of time t_0 as the time point at which the interaction L_I is switched on. We can then always take t_0 to be arbitrarily far into the past. For $t\leqslant t_0$ the reservoir is in its thermal-equilibrium state $\bar{\rho}_R$, and the system density operator $\rho_S(t)$ evolves independently of the reservoir. Therefore, we have for $t\leqslant t_0$

$$\rho(t)=\rho_S(t)\bar{\rho}_R. \tag{3.1}$$

Substitution into Eq. (2.11) and applying Eqs. (2.7) and (2.8) then shows that the term with $\rho(t_0)$ vanishes identically, due to the shift of the interaction Hamiltonian over its average. Then the equation of motion for $\rho_S(t)$ becomes

$$i\frac{d}{dt}\rho_S(t)=L_S\rho_S(t)-iTr_R L_I \times\int_{t_0}^{t}dt' e^{-i(L_S+L_R)(t-t')}L_I(\rho_S(t')\bar{\rho}_R), \tag{3.2}$$

for $t\geqslant t_0$.

Solving Eq. (3.2) is most easily done in the Laplace domain. If we define

$$\tilde{\rho}_S(\omega)=\int_{t_0}^{\infty}dt\, e^{i\omega(t-t_0)}\rho_S(t), \tag{3.3}$$

then the transformed equation of motion reads

$$(\omega-L_S)\tilde{\rho}_S(\omega)=i\rho_S(t_0)-i\,\mathrm{Tr}_R\,L_I \times[i/(\omega-L_S-L_R)] \times L_I(\tilde{\rho}_S(\omega)\bar{\rho}_R), \tag{3.4}$$

with solution

$$\tilde{\rho}_S(\omega)=[i/(\omega-L_S+i\tilde{\Gamma}(\omega))]\rho_S(t_0). \tag{3.5}$$

Here we introduced the relaxation operator $\tilde{\Gamma}(\omega)$ as

$$\tilde{\Gamma}(\omega)\sigma_S=\mathrm{Tr}_R\,L_I[i/(\omega-L_S-L_R)]L_I(\sigma_S\bar{\rho}_R), \tag{3.6}$$

which can equivalently be written as

$$\tilde{\Gamma}(\omega)\sigma_S=\mathrm{Tr}_R\,L_I\int_0^{\infty}d\tau\, e^{i(\omega-L_S-L_R)\tau}L_I(\sigma_S\bar{\rho}_R). \tag{3.7}$$

From Eq. (3.5) we see that $\tilde{\rho}_S(\omega)$, and thereby $\rho_S(t)$ for $t\geqslant t_0$, is determined by $\rho_S(t_0)$ only, and not by $\rho_S(t)$ for $t\leqslant t_0$. This is of course a result of assumption (3.1). The memory in the time evolution of $\rho_S(t)$ is displayed in the frequency dependence of $\tilde{\Gamma}(\omega)$. In the Appendix we show that $\tilde{\Gamma}(\omega)$ acquires a constant value (ω independent) in the Markov approximation.

From Eq. (3.7) we notice that $\tilde{\Gamma}(\omega)$ has the form of a Laplace transform

$$\tilde{\Gamma}(\omega)=\int_0^{\infty}d\tau\, e^{i\omega\tau}\Gamma(\tau), \tag{3.8}$$

where $\Gamma(\tau)$ is given by

$$\Gamma(\tau)\sigma_S=\mathrm{Tr}_R\,L_I e^{-i(L_S+L_R)\tau}L_I(\sigma_S\bar{\rho}_R), \tag{3.9}$$

for $\tau\geqslant 0$. Rewriting the equation of motion (3.2) in terms of $\Gamma(\tau)$ gives

$$i\frac{d}{dt}\rho_S(t)=L_S\rho_S(t)-i\int_{t_0}^{t}dt'\,\Gamma(t-t')\rho_S(t'), \tag{3.10}$$

which reveals that the time width of $\Gamma(\tau)$ (its decay time for $\tau\geqslant 0$) equals the memory time of the reservoir-interaction term. It is the width of $\Gamma(\tau)$ which is usually termed the reservoir correlation time τ_c. Then it follows from Eq. (3.8) that the frequency width of $\tilde{\Gamma}(\omega)$ is of the order of $1/\tau_c$, and for $\tau_c\to 0$, $\tilde{\Gamma}(\omega)$ becomes independent of ω.

The time evolution of $\rho_S(t)$ for $t\geqslant t_0$ will have little significance in general, which is partially due to the factorization at $t=t_0$. Due to the coupling to the reservoir, the density operator $\rho_S(t)$ will relax to a steady state (thermal equilibrium)

$$\bar{\rho}_S=\lim_{t\to\infty}\rho_S(t) \tag{3.11}$$

on a time scale $1/\Gamma$, as mentioned in the Introduction. Here, Γ denotes a typical matrix element of $\tilde{\Gamma}(\omega)$ [not of $\Gamma(\tau)$]. From the identity

$$\bar{\rho}_S=\lim_{\omega\to 0}\ -i\omega\tilde{\rho}_S(\omega) \tag{3.12}$$

and Eq. (3.5), we find the equation for $\bar{\rho}_S$ to be

$$(L_S-i\tilde{\Gamma}(0))\bar{\rho}_S=0. \tag{3.13}$$

This shows that the long-time solution of $\rho_S(t)$ is determined by $\tilde{\Gamma}(\omega)$ at $\omega=0$. Furthermore, we notice that the dependence on the initial value $\rho_S(t_0)$ has disappeared in Eq. (3.13), which reflects that the memory of the preparation of the system at t_0 is erased.

IV. CORRELATION FUNCTION

Measurement of the steady-state density operator $\bar{\rho}_S$ of a physical system is tantamount to the determination of its relaxation constants, which are the matrix elements of $\tilde{\Gamma}(0)$, as displayed in Eq. (3.13). Dynamical properties of the system in contact with the reservoir, however, are reflected in the time evolution of $\rho_S(t)$ before it reaches its steady state $\bar{\rho}_S$. In view of Eq. (3.5), this transient behavior of $\rho_S(t)$ is governed by the frequency dependence of the relaxation operator $\tilde{\Gamma}(\omega)$. Besides the fact that a density operator is not amenable to direct observation, we also see from Eq. (3.5) that the details of $\rho_S(t)$ depend on the preparation of the system at $t=t_0$. Obviously, it is impossible to fix $\rho_S(t_0)$ (say, the wave function of an atom) at a single instant of time, and subsequently measure its evolution for $t>t_0$.

A standard method of obtaining dynamical information about a system is by observation of steady-state correlation functions of system operators, say X and Y. If we take arbitrarily t_0 as the instant of time at which the Schrödinger and Heisenberg pictures coincide, then the time dependence of X is given by

$$X(t) = e^{iL(t-t_0)}X, \tag{4.1}$$

where L indicates the Liouvillian $L_S + L_R + L_I$ of the entire system. Then $X(t_0) = X$ is an operator in S space only, but for $t > t_0$, $X(t)$ is an operator in $S + R$ space, due to L_I. Hence the time evolution of $X(t)$ carries information on the interaction with the reservoir. The correlation function of two operators X and Y is defined as the expectation value

$$\langle\langle X(t')Y(t)\rangle\rangle = \operatorname{Tr}\rho(t_0)X(t')Y(t) \ . \tag{4.2}$$

The double-bracket notation indicates an average with the full density operator of $S + R$, rather than with $\bar{\rho}_R$ only [Eq. (1.5)]. Transformation of Eq. (4.2) to the Schrödinger picture gives

$$\langle\langle X(t')Y(t)\rangle\rangle = \operatorname{Tr} Ye^{-iL(t-t')}(\rho(t')X) , \tag{4.3}$$

or equivalently

$$\langle\langle X(t')Y(t)\rangle\rangle = \operatorname{Tr} Xe^{-iL(t'-t)}(Y\rho(t)) . \tag{4.4}$$

We notice that the initial time t_0 has disappeared in Eqs. (4.3) and (4.4), which already removes the ambiguities associated with the preparation of $\rho_S(t_0)$. A steady-state correlation function is now defined as $\langle\langle X(t')Y(t)\rangle\rangle$ with $t \gg t_0$, $t' \gg t_0$, and $t - t'$ fixed. Then the system is in state $\bar{\rho}_S$, which is time independent and a solution of Eq. (3.13). The time regression of the correlation functions (their $t - t'$ dependence) is governed by the same exponential that determines the time evolution of $\rho(t)$, and therefore we can extract dynamical properties of the system by an observation of the steady-state correlation functions.

Commonly, time regressions are not measured directly. For atoms or molecules on a solid substrate, for instance, one determines the spectral profile for the absorption of low-intensity monochromatic laser radiation with frequency ω. The spectral distribution as a function of ω and in the steady state is then given by expressions of the form

$$I(\omega) = \lim_{t\to\infty} \int_t^\infty dt'\, e^{i\omega(t'-t)}\langle\langle X(t')Y(t)\rangle\rangle, \tag{4.5}$$

which will further be referred to as the spectrum. It is the goal of this paper to evaluate $I(\omega)$ for a system in interaction with a finite memory-time reservoir.

V. SPECTRUM

From Eq. (4.5) we observe that we need the correlation function for $t' \geqslant t$, and therefore the representation (4.4) is most suitable. Then the occurring exponential is the same as for the time evolution of $\rho(t)$. If we introduce the Hilbert-space operator (Liouville-space vector)

$$A(t',t) = e^{-iL(t'-t)}(Y\rho(t)), \tag{5.1}$$

then the correlation function can be represented by

$$\langle\langle X(t')Y(t)\rangle\rangle = \operatorname{Tr}_S XA_S(t',t), \tag{5.2}$$

which only involves the system part $A_S(t',t) = \operatorname{Tr}_R A(t',t)$. In terms of the Laplace transform with respect to t',

$$\tilde{A}_S(\omega,t) = \int_t^\infty dt'\, e^{i\omega(t'-t)}A_S(t',t), \tag{5.3}$$

the spectrum attains the form

$$I(\omega) = \lim_{t\to\infty} \operatorname{Tr}_S X\tilde{A}_S(\omega,t) \ . \tag{5.4}$$

Differentiating Eq. (5.1) with respect to t' yields the equation of motion for $A(t',t)$,

$$i\frac{d}{dt'}A(t',t) = (L_S + L_R + L_I)A(t',t) \ , \tag{5.5}$$

which has to be solved for $t' \geqslant t$, with initial value

$$A(t,t) = Y\rho(t). \tag{5.6}$$

Equation (5.5) is identical to Eq. (2.5) for $\rho(t)$, and integrals can be found in the same way. The difference between a density operator and a correlation function is that for $\rho(t)$ we can choose the initial value $\rho(t_0)$ arbitrarily, whereas for $A(t',t)$ the initial value is unambiguously given by Eq. (5.6). This reflects the fact that $A(t',t)$ is essentially a two-time quantity. Its regression from t to t' is governed by Eq. (5.5) and its dependence on t enters through the initial condition, Eq. (5.6). The memory in the time regression, due to the finite reservoir correlation time, is of course the same as for the density operator and can be accounted for by the frequency-dependent relaxation operator $\tilde{\Gamma}(\omega)$, as we shall show below. As a second effect of a finite τ_c the density operator $\rho(t)$ in the initial value will carry a memory of its time evolution in the recent past. It is tempting to argue that we consider the steady state $t\to\infty$, so that the density operator $\rho(t)$ is constant in time. By the large-reservoir assumption we know that the reservoir remains in the state $\bar{\rho}_R$, whereas the system is in state $\bar{\rho}_S$ for $t\to\infty$. This would imply the replacement $\rho(t)\to\bar{\rho}_S\bar{\rho}_R$ in Eq. (5.6), which in turn would eliminate the explicit t dependence of $A(t',t)$, making the limit $t\to\infty$ in Eq. (5.4) trivial. We shall show that this procedure cannot be justified if τ_c is finite.

Since Eq. (5.5) is identical to Eq. (2.5) for $\rho_S(t)$, we can derive the appropriate integral along the same lines. The analog of Eq. (2.11) is

$$i\frac{d}{dt'}A_S(t',t) = L_SA_S(t',t) + \operatorname{Tr}_R L_Ie^{-i(L_S+L_R)(t'-t)}(Y\rho(t)) - i\operatorname{Tr}_R L_I\int_t^{t'} dt''\, e^{-i(L_S+L_R)(t'-t'')}L_I(A_S(t'',t)\bar{\rho}_R) , \tag{5.7}$$

which contains $\rho(t)$ explicitly. Now we can substitute the right-hand side of Eq. (2.9) for $\rho(t)$ and take for $\rho(t_0)$ the value of $\rho_S(t_0)\bar{\rho}_R$. Then Eq. (5.7) becomes

$$
\begin{aligned}
i\frac{d}{dt'}A_S(t',t) = {} & L_S A_S(t',t) + \mathrm{Tr}_R\, L_I e^{-i(L_S+L_R)(t'-t)} L_Y e^{-i(L_S+L_R)(t-t_0)}(\rho_S(t_0)\bar{\rho}_R) \\
& - i\,\mathrm{Tr}_R\, L_I e^{-i(L_S+L_R)(t'-t)} L_Y \int_{t_0}^{t} dt''\, e^{-i(L_S+L_R)(t-t'')} L_I \rho(t'') \\
& - i\,\mathrm{Tr}_R\, L_I \int_{t}^{t'} dt''\, e^{-i(L_S+L_R)(t'-t'')} L_I (A_S(t'',t)\bar{\rho}_R)\,, \qquad (5.8)
\end{aligned}
$$

where we introduced the Liouvillian L_Y by

$$L_Y \sigma_S = Y\sigma_S, \qquad (5.9)$$

in order to avoid notations with too many brackets. In the second term on the right-hand side of Eq. (5.8), the exponentials with L_R act only on $\bar{\rho}_R$, because L_R commutes with L_S and L_Y. Therefore they cancel, according to Eq. (2.7). The remaining two exponentials and L_Y affect only $\rho_S(t_0)$, and the result is some operator σ_S in S space. With Eq. (2.8) we then find that the whole term is identically zero. Considering the third term on the right-hand side, we notice that it has the form of a reservoir integral, as in Eq. (2.10), which implies that we can factorize $\rho(t'')$ here. Then we define a "density operator" $\rho_{SR}(t)$ of $S+R$ space by

$$\rho_{SR}(t) = \int_{t_0}^{t} dt'\, e^{-i(L_S+L_R)(t-t')} L_I(\rho_S(t')\bar{\rho}_R)\,, \qquad (5.10)$$

which allows us to write Eq. (5.8) as

$$
\begin{aligned}
i\frac{d}{dt'}A_S(t',t) = {} & L_S A_S(t',t) \\
& - i\,\mathrm{Tr}_R\, L_I e^{-i(L_S+L_R)(t'-t)} L_Y \rho_{SR}(t) \\
& - i\,\mathrm{Tr}_R\, L_I \int_{t}^{t'} dt''\, e^{-i(L_S+L_R)(t'-t'')} \\
& \times L_I(A_S(t'',t')\bar{\rho}_R)\,. \qquad (5.11)
\end{aligned}
$$

Next we take the Laplace transform of Eq. (5.11), recalling that

$$A_S(t,t) = L_Y \rho_S(t)\,, \qquad (5.12)$$

as follows from Eq. (5.6), and rearrange the terms. We then obtain

$$
\begin{aligned}
\tilde{A}_S(\omega,t) = {} & \frac{i}{\omega - L_S + i\tilde{\Gamma}(\omega)} \Big\{ L_Y \rho_S(t) \\
& - \mathrm{Tr}_R\, L_I \frac{i}{\omega - L_S - L_R} L_Y \rho_{SR}(t) \Big\}\,. \qquad (5.13)
\end{aligned}
$$

The factor in front of the curly brackets is the same as in Eq. (3.5), and it represents the time regression from t to t' of $A_S(t',t)$. The first term inside the curly brackets, $L_Y\rho_S(t)$, corresponds to a factorized initial state. If we would have replaced $A(t,t) = Y\rho(t)$ by $Y(\rho_S(t)\bar{\rho}_R)$, then it is easy to see that the second term on the right-hand side of Eq. (5.7) would have disappeared, and thereby the second term in curly brackets in Eq. (5.13). Conversely, the term with $\rho_{SR}(t)$ in Eq. (5.13) accounts for the correlations between S and R in $\rho(t)$, which are present at the initial time for the time evolution of $A(t',t)$ from t to t'.

The explicit time dependence of $\tilde{A}_S(\omega,t)$ enters through $\rho_S(t)$ and $\rho_{SR}(t)$. If we denote their steady-state values by an overbar, then the spectrum, Eq. (5.4), becomes

$$
\begin{aligned}
I(\omega) = {} & \mathrm{Tr}_S\, L_X \frac{i}{\omega - L_S + i\tilde{\Gamma}(\omega)} \\
& \times \Big\{ L_Y \bar{\rho}_S - \mathrm{Tr}_R\, L_I \frac{i}{\omega - L_S - L_R} L_Y \bar{\rho}_{SR} \Big\}\,, \qquad (5.14)
\end{aligned}
$$

with

$$L_X \sigma_S = X\sigma_S. \qquad (5.15)$$

Expression (5.14) involves the system-reservoir state $\bar{\rho}_{SR}$, which might seem cumbersome. From Eq. (5.10) we find the Laplace transform of $\rho_{SR}(t)$ to be

$$\tilde{\rho}_{SR}(\omega) = [i/(\omega - L_S - L_R)]L_I(\tilde{\rho}_S(\omega)\bar{\rho}_R)\,, \qquad (5.16)$$

in terms of $\tilde{\rho}_S\omega$ from Eq. (3.5). Then the steady-stae $\bar{\rho}_{SR}$ follows from the identity (3.12), which gives

$$\bar{\rho}_{SR} = [i/(i0^+ - L_S - L_R)]L_I(\bar{\rho}_S\bar{\rho}_R)\,. \qquad (5.17)$$

Here, the notation $i0^+$ indicates a small positive imaginary part, which is necessary to assure the convergence of Laplace-transform integrals, or equivalently, the existence of the inverse of $i0^+ - L_S - L_R$. In the next section we show how to evaluate the right-hand side of Eq. (5.17). If we define an operator $\tilde{\Upsilon}(\omega)$ by

$$
\begin{aligned}
\tilde{\Upsilon}(\omega)\sigma_S = {} & \mathrm{Tr}_R\, L_I \frac{i}{\omega - L_S - L_R} \\
& \times L_Y \frac{1}{i0^+ - L_S - L_R} L_I(\sigma_S\bar{\rho}_R)\,, \qquad (5.18)
\end{aligned}
$$

then the spectrum attains the form

$$I(\omega) = \mathrm{Tr}_S\, L_X[i/(\omega - L_S + i\tilde{\Gamma}(\omega))](L_Y - i\,\tilde{\Upsilon}(\omega))\bar{\rho}_S. \qquad (5.19)$$

Equation (5.19) is the most condensed and general representation of the result of this paper. The finite memory time of the reservoir appears as a frequency dependence of the relaxation operator $\tilde{\Gamma}(\omega)$, and as a nonvanishing initial-correlation operator $\tilde{\Upsilon}(\omega)$.

VI. $\mathcal{S}\mathcal{R}$ INTERACTION

Although the result (5.19) is appealing and explicit, the occurring operators $\tilde{\Gamma}(\omega)$ and $\tilde{\Upsilon}(\omega)$, which represent the interaction of the system with reservoir, might look awkward in their definitions, Eqs. (3.6) and (5.18). Especially the reservoir Liouvillian L_R in denominators and the appearance of $i0^+$ in Eq. (5.18) might seem to make an explicit evaluation of $\tilde{\Gamma}(\omega)$ and $\tilde{\Upsilon}(\omega)$ intractable. Such is, however, not the case, as we shall show in this section.

Obviously, an elaboration of $\widetilde{\Gamma}(\omega)$ and $\widetilde{\Upsilon}(\omega)$ requires additional specifications of the interaction Hamiltonian H_I. It will turn out to be sufficient to assume the form

$$H_I = \hbar \sum_k \mathscr{S}_k \mathscr{R}_k, \tag{6.1}$$

with $\mathscr{S}_k$ $(\mathscr{R}_k)$ a pure S (R) operator. The form (6.1) pertains to most practical situations we have encountered. In the case of fluorescence, $\mathscr{S}_k$ signifies the k th Cartesian component of the atomic dipole moment, and for adsorbates on a substrate the subscript k takes on two values, corresponding to the two terms in the binding (Morse) potential. In fact, the form (6.1) for H_I can always be enforced by an expansion in matrix elements.

Evaluation of the relaxation operator $\widetilde{\Gamma}(\omega)$ starts from its representation (3.9) in the time domain. We expand the two L_I's as commutators, which gives rise to four terms. Then we insert H_I from Eq. (6.1), and we notice that every factor is an operator in S or R space only. Combining the R operators and taking the trace over the reservoir states then shows that the R contribution can be accounted for by a single complex-valued function

$$f_{kl}(\tau) = \langle \mathscr{R}_k e^{-iL_R\tau} \mathscr{R}_l \rangle, \tag{6.2}$$

which will be called the reservoir correlation function. We find

$$\Gamma(\tau)\sigma_S = \sum_{kl} L_l e^{-iL_S\tau} (f_{lk}(\tau) \mathscr{S}_k \sigma_S - f^*_{lk}(\tau) \sigma_S \mathscr{S}_k), \tag{6.3}$$

with

$$L_l \sigma_S = [\mathscr{S}_l, \sigma_S] . \tag{6.4}$$

Expression (6.3) only involves the system operators $\mathscr{S}_k$ and the Liouvillian L_S for the free evolution of the system. The reservoir enters via the parameter functions $f_{kl}(\tau)$, which can be found as soon as a particular reservoir is prescribed. For a harmonic crystal, for instance, the reservoir correlation functions are given analytically in Ref. 17.

The initial correlation operator $\widetilde{\Upsilon}(\omega)$ from Eq. (5.18) is the Laplace transform of

$$\begin{aligned}\Upsilon(\tau)\sigma_S = {} & \mathrm{Tr}_R\, L_I e^{-i(L_S + L_R)\tau} \\ & \times L_Y [1/(i0^+ - L_S - L_R)] L_I(\sigma_S \bar{\rho}_R) .\end{aligned} \tag{6.5}$$

First we recall that the notation $i0^+$ should be read as

$$\begin{aligned}& \frac{1}{i0^+ - L_S - L_R} L_I(\sigma_S \bar{\rho}_R) \\ & \quad = -i \lim_{\omega \to i0^+} \int_0^\infty d\tau' e^{i(\omega - L_S - L_R)\tau'} L_I(\sigma_S \bar{\rho}_R) .\end{aligned} \tag{6.6}$$

Then we insert the form (6.1) for the interaction and rearrange the S and R terms. We then obtain for $\Upsilon(\tau)$

$$\begin{aligned}\Upsilon(\tau)\sigma_S = {} & i \sum_{kl} L_l e^{-iL_S\tau} L_Y \int_o^\infty dt' e^{-iL_S\tau'} \\ & \times (f_{lk}(\tau + \tau') \mathscr{S}_k \sigma_S - f^*_{lk}(\tau + \tau') \sigma_S \mathscr{S}_k) ,\end{aligned} \tag{6.7}$$

where the reservoir is again entirely incorporated in the functions $f_{kl}(\tau)$. Since the $f_{lk}(\tau)$'s decay to zero sufficiently fast for $\tau \to \infty$, we omitted at this stage the $i0^+$ in the rightmost exponential.

VII. LAPLACE TRANSFORM

Before we can take the Laplace transform of Eqs. (6.3) and (6.7), we must work out the exponentials. Eigenstates of the system Hamiltonian will be denoted by $|a,\alpha\rangle$, where a indicates the energy and α any degeneracy. By definition they obey

$$H_S |a,\alpha\rangle = \hbar\omega_a |a,\alpha\rangle. \tag{7.1}$$

With respect to its own eigenstates we can write H_S as

$$H_S = \sum_{a,\alpha} \hbar\omega_a |a,\alpha\rangle\langle a,\alpha| = \sum_a \hbar\omega_a P_a, \tag{7.2}$$

with

$$P_a = \sum_\alpha |a,\alpha\rangle\langle a,\alpha|, \tag{7.3}$$

the projector on the subspace with energy $\hbar\omega_a$. From the orthonormality of the states $|a,\alpha\rangle$ we have

$$P_a P_b = \delta_{ab} P_a, \tag{7.4}$$

and from the completeness of the set $|a,\alpha\rangle$ we find the closure relation

$$\sum_a P_a = 1. \tag{7.5}$$

Then it is an easy matter to expand the exponential $\exp(-iL_S\tau)$ in projectors, which gives

$$e^{-iL_S\tau}\sigma_S = \sum_{ab} e^{-i\Delta_{ab}\tau} P_a \sigma_S P_b, \tag{7.6}$$

in terms of the level separations

$$\Delta_{ab} = \omega_a - \omega_b. \tag{7.7}$$

Next we substitute Eq. (7.6) into Eq. (6.3) and evaluate the Laplace transform. We obtain

$$\begin{aligned}\widetilde{\Gamma}(\omega)\sigma_S = {} & \sum_{kl} L_l \sum_{ab} P_a (\tilde{f}_{lk}(\Delta_{ba} + \omega) \mathscr{S}_k \sigma_S \\ & - \tilde{f}^*_{lk}(-\Delta_{ba} - \omega) \sigma_S \mathscr{S}_k) P_b,\end{aligned} \tag{7.8}$$

in terms of the Laplace transform $\tilde{f}_{kl}(\omega)$ of $f_{kl}(\tau)$. Because L_l equals the commutator with $\mathscr{S}_l$, the right-hand side only involves operators $\mathscr{S}_l$ and projectors. If we insert the closure relation (7.5) in various places in Eq. (7.8), we immediately find the matrix representation of $\widetilde{\Gamma}(\omega)$ in terms of matrix elements of $\mathscr{S}_l$. The result (7.8) is the most compact representation of the explicit form of $\widetilde{\Gamma}(\omega)$.

In the very same way we find the Laplace transform of $\Upsilon(\tau)$ from Eq. (6.7), although with considerably more effort, which is due to the double integral (over τ and τ'). The result is

$$\begin{aligned}\tilde{\Upsilon}(\omega)\sigma_S = \sum_{kl} L_l \sum_{abc} \frac{1}{\Delta_{ac}+\omega} P_c Y P_a \\ \times\{(\tilde{f}_{lk}(\Delta_{ba}) - \tilde{f}_{lk}(\Delta_{bc}+\omega))\mathscr{S}_k\sigma_S \\ -(\mathscr{S}f^*_{lk}(-\Delta_{ba}) \\ -\mathscr{S}f^*_{lk}(-\Delta_{bc}-\omega))\sigma_S\mathscr{S}_k\}P_b,\end{aligned} \tag{7.9}$$

which has a striking resemblance with Eq. (7.8). Most remarkable is that $\tilde{\Upsilon}(\omega)$ can again be expressed in the reservoir correlation function $\tilde{f}_{kl}(\omega)$ which also determines $\tilde{\Gamma}(\omega)$, and, as shown in the Appendix, the relaxation operator in the Markov approximation. The distinction is that the functions $\tilde{f}_{kl}(\omega)$ occur with different arguments.

If ω equals a level separation $\Delta_{ca} = -\Delta_{ac}$, then the denominator of the first factor under the triple summation in Eq. (7.9) becomes zero. For $\omega = \Delta_{ca}$ we have $\Delta_{bc} + \omega = \Delta_{ba}$, and hence the difference of the two functions $\tilde{f}_{lk}$ in curly brackets also approaches zero. In the process of deriving Eq. (7.9) we found that this feature does not constitute a problem. The limit is simply

$$\begin{aligned}\lim_{\omega\to-\Delta_{ac}} \frac{1}{\Delta_{ac}+\omega}(\tilde{f}_{lk}(\Delta_{ba}) - \tilde{f}_{lk}(\Delta_{bc}+\omega)) \\ = -\frac{d}{d\omega}\tilde{f}_{lk}(\omega), \quad \text{in } \omega = \Delta_{ba},\end{aligned} \tag{7.10}$$

and there is no singularity or discontinuity if ω passes across a resonance.

VIII. CONCLUSIONS

If the decay time τ_c of the reservoir correlation function $f_{kl}(\tau)$ for $\tau\to\infty$ is not small in comparison with the relaxation times $1/\Gamma$, which are determined by the same function [see Eq. (7.8)], then a Markov approximation cannot be correct. In this paper we imposed no limits on τ_c. We only assumed that the system S is small in comparison with the reservoir R. The finite value of τ_c amounts to a memory in the time evolution of the density operator, which is reflected in a frequency dependence of the relaxation operator $\tilde{\Gamma}(\omega)$. Correlation functions of system operators depend on two times, t' and t. The regression from t to t' exhibits the same memory effect as the time evolution of the density operator. Additionally, the equal-time correlation function, which is the initial value for the time regression, carries a memory to the recent past. It appears that this second phenomenon could be accounted for by an initial correlation operator $\tilde{\Upsilon}(\omega)$ in the expression for the spectrum $I(\omega)$.

Frequency-dependent relaxation operators are widely applied in the literature. Their Laplace inverse $\Gamma(\tau)$ is sometimes called a memory kernel, because it is the finite time width of $\Gamma(\tau)$ which brings about the memory in the time evolution, as is most obvious from Eq. (3.10). Initial-correlation operators, however, are rare.[18] Despite the fact that the frequency dependence of $\tilde{\Gamma}(\omega)$ originates from the same memory mechanism which amounts to a nonvanishing $\tilde{\Upsilon}(\omega)$, the latter is usually not found. As pointed out in the derivation of $\tilde{\Upsilon}(\omega)$, the disappearance of $\tilde{\Upsilon}(\omega)$ is a consequence of a factorization of the initial value or state, which cannot be justified in general.

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APPENDIX: MARKOV APPROXIMATION

It is illuminating to compare the results of the present paper with their equivalents under the Markov approximation. Since we already have Eq. (2.11) we can start here. First, we state that we are not interested in a time evolution of $\rho_S(t)$ on a time scale τ_c, which implies that we can factorize $\rho(t_0)$ as $\rho_S(t_0)\bar{\rho}_R$. In this fashion we discard the memory of the initial state to its past, which immediately gives $\tilde{\Upsilon}(\omega)\equiv 0$, or equivalently, the second term on the right-hand side of Eq. (2.11) is zero. Second, we know that if we work out the integral in Eq. (2.11), we find reservoir correlation functions $f_{kl}(t-t')$, which decay to zero on a time scale τ_c. Therefore, the major contribution to the integral comes from $t-\tau_c \lesssim t' \leqslant t$. Because we impose the condition $\Gamma\tau_c \ll 1$, the density operator $\rho_S(t')$ in the integrand is not affected significantly by the relaxation process on this small time interval. Then we can replace $\rho_S(t')$ by its free evolution

$$\rho_S(t') = e^{-iL_S(t'-t)}\rho_S(t), \tag{A1}$$

and subsequently take $\rho_S(t)$ outside the integral. Third, according to the first assumption we can take $t - t_0 \gg \tau_c$, which gives in combination with the fact that the integrand is only nonzero on a time interval τ_c that we can replace t_0 by minus infinity. Combining everything then yields

$$i\frac{d}{dt}\rho_S(t) = (L_S - i\Gamma_M)\rho_S(t)\,, \tag{A2}$$

with

$$\Gamma_M\sigma_S = \mathrm{Tr}_R\, L_I \int_0^\infty d\tau\, e^{-i(L_S+L_R)\tau} L_I e^{iL_S\tau}(\sigma_S\bar{\rho}_R)\,. \tag{A3}$$

The Laplace transform of Eq. (A3) reads

$$\tilde{\rho}_S(\omega) = [i/(\omega - L_S + i\Gamma_M)]\rho_S(t_0)\,, \tag{A4}$$

and comparison with Eq. (3.5) then shows that Γ_M is the Markovian equivalent of $\tilde{\Gamma}(\omega)$, and indeed, the frequency dependence has disappeared.

There exists an interesting relation between Γ_M and $\tilde{\Gamma}(\omega)$, which can be found as follows. In Eq. (3.9) we substitute $\exp(iL_S\tau)\sigma_S$ for σ_S and integrate the result over τ. With Eq. (A3) we then obtain

$$\Gamma_M = \int_0^\infty d\tau\, \Gamma(\tau)e^{iL_S\tau}, \tag{A5}$$

as an operator identity. Then we notice that Eq. (3.8) can be inverted as

$$\Gamma(\tau) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega\tau}\tilde{\Gamma}(\omega)\,, \tag{A6}$$

for $\tau > 0$. Substitution into Eq. (A5) and performing the τ integration then leads to

$$\Gamma_M = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, \tilde{\Gamma}(\omega)\, \frac{i}{L_S - \omega}. \tag{A7}$$

With the projectors of Sec. VII we can write $L_S - \omega$ as

$$(L_S - \omega)\sigma_S = \sum_{ab} (\Delta_{ab} - \omega) P_a \sigma_S P_b, \tag{A8}$$

and taking matrix elements of both sides gives

$$\langle a,\alpha | ((L_S - \omega)\sigma_S) | b,\beta \rangle = (\Delta_{ab} - \omega) \langle a,\alpha | \sigma_S | b,\beta \rangle. \tag{A9}$$

This shows that the Liouvillian $L_S - \omega$ is diagonal with respect to the eigenstates of H_S, and that its matrix elements are $\Delta_{ab} - \omega$. Therefore, its inverse $1/(L_S - \omega)$ has corresponding matrix elements $1/(\Delta_{ab} - \omega)$, which gives the expansion of $1/(L_S - \omega)$ in projectors as

$$\frac{1}{L_S - \omega} \sigma_S = \sum_{ab} \frac{1}{\Delta_{ab} - \omega} P_a \sigma_S P_b. \tag{A10}$$

If we insert this into Eq. (A7) and remember the general property

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{i}{\omega - \omega'} \tilde{g}(\omega') = \tilde{g}(\omega), \tag{A11}$$

for any Laplace transform $\tilde{g}(\omega)$, we finally obtain

$$\Gamma_M \sigma_S = \sum_{ab} \tilde{\Gamma}(\Delta_{ab}) (P_a \sigma_S P_b). \tag{A12}$$

Another way to derive Eq. (A12) is by substituting the expansion (7.6) for $\exp(iL_S\tau)$ into Eq. (A5) and performing the τ integration. Equation (A12) reveals that the relaxation operator in the Markov approximation effectively filters out these ω values in $\tilde{\Gamma}(\omega)$ which are in exact resonance with the system frequencies.

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