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C. K. Chan and D. J. Kouri

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Sudden representation and sudden approximation quantal generalized master equation[a)]

C. K. Chan and D. J. Kouri
Department of Chemistry and Department of Physics, University of Houston, University Park, Houston, Texas 77004

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The application of the sudden approximation in the derivation of a quantal generalized master equation (GME) is examined. Two different types of physical systems are considered. One is a composite system comprised of a fast primary system and slow bath compared to the time the former is coupled to the latter. The other is a composite system comprised of a slow primary system and fast bath. The resulting sudden GME's for both cases contain non-Markovian memory kernels. In the second case, the memory kernel can be further approximated by a Markovian form. The resulting Markovian-sudden GME is identical to the GME obtained by using the adiabatic elimination method for removing the (fast) stochastic bath coordinates. Using a representation of the Schrödinger propagator for the density operator analogous to the recently developed (energy) sudden representation of the Schrödinger propagator for the wave function, the exact GME is recast into a form such that when the memory kernel and the inhomogeneity term of the equation are expanded in a perturbation series, the zeroth order equation is in the sudden approximation form. Finally, a harmonic oscillator coupled linearly to a bath of harmonic oscillators is used as an illustration. The behavior of the bath correlation functions in the Markovian and the sudden limits is examined. The reduction of the exact GME to the sudden approximation form is also considered.

I. INTRODUCTION

In quantal systems in which several subsystems are coupled together, under many circumstances, only some subset of each composite system is of detailed interest. Consequently, one would like to follow the dynamics of the primary system(s) in detail and to treat the other system(s) as a bath coupled to the primary one(s). To obtain the information on the primary system alone under the influence of its bath, one can formally eliminate the irrelevant bath coordinates. A variety of techniques of completely different nature can be used for this elimination. In this paper, we will focus on the projection operator techniques of Nakajima[1] and Zwanzig[2] and the (resulting) so-called generalized master equations (GME).[3,4]

In the Nakajima–Zwanzig theory, the elimination procedure is carried out using the Schrödinger picture of quantum mechanics. The starting point is the Liouville–von Neumann equation of motion for the density operator W of the composite system (primary system P + bath B):

$$\frac{\partial W}{\partial t} = -i/\hbar[H,W(t)] = -iLW(t), \tag{1.1}$$

where H and L denote the full Hamiltonian and the corresponding Liouvillian, respectively. To extract the information on P, a certain projection operator $\mathscr{P}$ (i.e., $\mathscr{P}^2 = \mathscr{P}$) is used such that when $\mathscr{P}$ acts on W, the reduced density operator ρ of P is obtained[3]

$$\mathscr{P}W = B_{\rm ref}\,{\rm Tr}_B\,W = B_{\rm ref}\,\rho. \tag{1.2}$$

Here Tr_B is the trace operation over the bath states and $B_{\rm ref}$ is any arbitrary reference state (density operator) of B satisfying the normalization constraint $\mathrm{Tr}_B\,B_{\rm ref} = 1$. Usually, $B_{\rm ref}$ is chosen to be the equilibrium density operator of B.[5] (This choice of $B_{\rm ref}$ leads to simpler expressions for the GME. This is especially crucial in our treatment throughout this paper.) Once ρ is known, the dynamics of P is completely determined since the expectation value of any operator A in P is given by $\langle A\rangle = \mathrm{Tr}_P\,\mathrm{Tr}_B\,WA = \mathrm{Tr}_P\,\rho A$, where Tr_P is the trace operation over the primary system states. Using $\mathscr{P}$, an equation of motion for the reduced density operator ρ of P can be obtained in the form[3,4]

$$\frac{\partial\rho}{\partial t} = -iL_{\rm eff}\,\rho(t) + \int_0^t dt'K(t,t')\rho(t') + I(t). \tag{1.3}$$

The first term depends only on the density operator at time t. It is the Markovian part of the rate of change of ρ (i.e., it does not depend on the past history) under the effective Liouvillian $L_{\rm eff}$. The second term depends on all previous $\rho(t')$, where t' ranges from the initial time 0 to the final time t. Hence, it represents the non-Markovian or memory effects. The integral kernel $K(t,t')$ is known as the memory kernel. The third term is the inhomogeneity $I(t)$ which depends on the initial conditions of the bath. If P and B are initially uncorrelated, then $I(t)$ is identically zero.

Equation (1.3) is known as the generalized master equation (GME). This equation, which is exact, is an integro-differential equation. Because of the rather involved formal expressions for the kernel (and the inhomogeneity term for initially correlated systems), the exact solution for the GME is impossible to find, and some form of approximation has to be introduced. In general, series expansions for K (and I) are normally used and only the first few terms are kept. The lowest order of the perturbation expansion is known as the Born approximation.[3,4,6,7] In this approximation, the memory kernel is second order in the interaction between P and

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B. A further approximation is to introduce the Markovian condition which reduces the GME to a partial differential equation[3]

$$\frac{\partial \rho}{\partial t} = -i\Lambda\rho(t) \tag{1.4}$$

with

$$\Lambda = L_{\text{eff}} + i\int_0^\infty dt\, K(t). \tag{1.5}$$

The Markovian approximation is adequate when B relaxes on a time scale which is much shorter than that of ρ (or P).

In the present work, we shall discuss the use of the sudden approximation[8] in the GME. Traditionally, this approximation has been used for studying collision problems.[9] Recently, the approximation has been used in a more general context, in particular, in studying bath effects using a path integral formalism.[10]

We first briefly discuss the features of the sudden approximation which are relevant to our later development. In the sudden approximation, one set of degrees of freedom (coordinates) is assumed to be slow compared to the rest. For example, the bath coordinates may be the slow coordinates (and the primary system coordinates the fast coordinates).[10] Let H_1 be the Hamiltonian corresponding to the slow coordinates. In this approximation, H_1 is assumed to commute with the coupling potential between the slow and the fast coordinates. [This is equivalent to saying that the (unperturbed) states of H_1 are degenerate. Hence, H_1 can be assumed to be a constant in the approximation.] We will show how this commutation condition simplifies the memory kernel in the GME.

Instead of applying the sudden approximation to systems with slow bath and fast primary system coordinates, the approximation can be applied to systems with fast bath and slow primary system coordinates. The resulting sudden GME's (obtained by using the commutation assumption mentioned earlier) in both cases possess memory kernels which are non-Markovian in form. In the second case of fast bath and slow primary system coordinates, the Markovian approximation can be applied subsequently to simplify the memory kernel further by assuming that the bath will relax on a time scale which is much shorter than that of the primary system. If the interaction between P and B in the memory kernel is kept just to the second order, the resulting Markovian-sudden GME is identical to the GME obtained from using the adiabatic elimination method in removing the (fast) stochastic bath coordinates.[11,12]

The exact GME can be recast into a form which has the sudden approximation as the zeroth order limit when the memory kernel and the inhomogeneity are expanded in a perturbation series. This can be accomplished easily by first removing the unperturbed motion of either P or B, which is designated to be slow in the sudden limit, from the full density operator using a unitary transformation. Applying the techniques of Nakajima and Zwanzig to the equation of motion in this "interaction picture" gives the desired GME. This interaction picture or representation for the (Schrödinger) evolution operator $\exp(-iLt)$ is *similar* to the sudden representation developed recently by Chang *et al.*[13] for the evolution operator $\exp(-i/\hbar Ht)$ in scattering problems. This alternative form of GME will be referred to as the sudden representation GME. Although this sudden representation GME is formally more complicated, the equation and in particular, its perturbation expansion, may be useful for (composite) systems with an appreciable degree of suddenness.

This paper is organized as follows. In Sec. II, we discuss the sudden approximation to the GME. The two different sudden limit cases mentioned above (i.e., either P or B has the slow coordinates) are discussed in detail. The sudden representation of the exact GME is derived next in Sec. III. In Sec. IV, a well-known simple model, used commonly in quantum optics, of a damped harmonic oscillator is used to illustrate the form of the different (approximate) GME's. For simplicity, the heat bath is assumed to be made up of harmonic oscillators. Not all of the results are new but are included for completeness. The behavior of the bath correlation functions in the Markovian and the sudden limits (for the fast and the slow bath, respectively) is examined. The reduction from the exact to the sudden GME is also considered for this model. Finally, in Sec. V, we discuss briefly possible applications of the sudden GME to collision problems with multiple time scales.

II. SUDDEN APPROXIMATION GME

The subject of the GME has been discussed and reviewed extensively.[1–4,11,14] Here, we first briefly review its derivation and the Born and Markovian approximations thereto. The sudden GME can be readily obtained by imposing the commutation assumption of the sudden approximation on the exact GME.

The Hamiltonian H and the corresponding Liouvillian L for the composite system $P+B$ are given by

$$H = H_P + H_B + V_{PB}, \tag{2.1}$$

$$L = L_P + L_B + L_{PB}, \tag{2.2}$$

where $X_{P(B)}$ refers to the free motion of $P(B)$ and X_{PB} the interaction of P with B. Using the formal solution of Eq. (1.1), the Liouville–von Neumann equation for the full density operator W can be written in the form

$$\frac{\partial W}{\partial t} = -iL\exp(-iLt)W(0). \tag{2.3}$$

For the time being, let $\mathcal{P}$ and $\mathcal{Q}$ be *any* time independent operators related by

$$\mathcal{P} + \mathcal{Q} = 1. \tag{2.4}$$

Using $\mathcal{P}$ and $\mathcal{Q}$, the time evolution operator (for the density operator) in the Schrödinger representation can be written in the form[14]

$$\exp(-iLt) = \mathcal{P}\exp(-iLt) - \int_0^t dt' \times \exp[-i\mathcal{Q}L(t-t')]\mathcal{Q}iL\mathcal{P} \times \exp(-iLt') + \exp(-i\mathcal{Q}Lt)\mathcal{Q}. \tag{2.5}$$

The identity holds for any time-independent operators L, and $\mathcal{P}$ and $\mathcal{Q}$ [satisfying the condition of (2.4)].

From now on, we restrict $\mathscr{P}$ to be the projection operator defined in Eq. (1.2) and $\mathscr{Q}$ is its complement. Let X be any arbitrary operator. $\mathscr{P}$ satisfies the identities

$$\mathscr{P}L_B\,X=0, \tag{2.6}$$

$$\mathscr{P}L_P\,X=L_P\,\mathscr{P}X, \tag{2.7}$$

which follow from the cyclic invariance of the trace operation and the commutativity of operators in different spaces. We also choose $B_{\rm ref}$ to be the equilibrium density operator of the bath B, i.e., $B_{\rm ref}=\rho_{\rm B}=\exp(-\beta H_B)/{\rm Tr}_B\exp(-\beta H_B)$. In this case, we also have

$$L_B\,\mathscr{P}X=0. \tag{2.8}$$

The decomposition of the evolution operator in Eq. (2.5) using the projection operators $\mathscr{P}$ and $\mathscr{Q}$ has physical relevance.[14,15] This will be apparent shortly.

Now, applying $\mathscr{P}$ to Eq. (2.3) and using Eq. (2.5), we arrive at the GME of (1.3) with[3,16]

$$\begin{aligned}L_{\rm eff}&={\rm Tr}_B\,L\rho_B\\&=L_P+{\rm Tr}_B\,L_{PB}\,\rho_B,\end{aligned} \tag{2.9}$$

$$\begin{aligned}K(t,t')&=-{\rm Tr}_B\,L\exp[-i\mathscr{Q}L(t-t')]\mathscr{Q}L\rho_B\\&=-{\rm Tr}_B\,L_{PB}\exp[-i(L_P+L_B\\&\quad+\mathscr{Q}L_{PB})(t-t')]\mathscr{Q}L_{PB}\,\rho_B,\end{aligned} \tag{2.10}$$

$$\begin{aligned}I(t)&=-i\,{\rm Tr}_B\,L\exp(-i\mathscr{Q}Lt)\mathscr{Q}W(0)\\&=-i\,{\rm Tr}_B\,L_{PB}\exp[-i(L_P+L_B\\&\quad+\mathscr{Q}L_{PB})t\,]\mathscr{Q}W(0).\end{aligned} \tag{2.11}$$

The second equalities in Eqs. (2.9)–(2.11) follow from the identities (2.6)–(2.8).

In the usual applications of the GME in quantum optics, $\mathscr{P}$ is assumed to satisfy the condition[3,4,6,7,16]

$$\mathscr{P}L_{PB}\,\mathscr{P}X=0 \tag{2.12}$$

which is satisfied when

$${\rm Tr}_B\,V_{PB}\,\rho_B=0. \tag{2.13}$$

The quantity ${\rm Tr}_B\,V_{PB}\,\rho_B$ corresponds to the mean *conservative* force exerted on P by B. This can be assumed to vanish or simply be incorporated into H_P and H_B.[3,16] [For some forms of V_{PB}, Eqs. (2.12) and (2.13) are exact. See Sec. IV.] Using the assumption of Eq. (2.12), $L_{\rm eff}$ and K become

$$L_{\rm eff}=L_P, \tag{2.14}$$

$$\begin{aligned}K(t,t')&=-{\rm Tr}_B\,L_{PB}\exp[-{\rm i}(L_P+L_B\\&\quad+\mathscr{Q}L_{PB})(t-t')]L_{PB}\,\rho_B.\end{aligned} \tag{2.16}$$

For initially uncorrelated P and B, we have $W(0)=\rho_B\,\rho(0)=\mathscr{P}W(0)$. This implies $I(t)\equiv 0$. Here, we have assumed B to be initially in equilibrium.

Under many circumstances, the bath is a large system with relaxation time τ_B much shorter than that of P. For $t\gg\tau_B$, the memory kernel K [and $I(t)$], which relaxes on the same time scale as τ_B, can be treated as a very rapidly decaying function(s). If this is true, the Markovian GME of Eq. (1.4) is expected to hold since the effective range of integration is determined by the memory kernel which vanishes after a very short time over which ρ has not changed much. Hence, the fluctuations of P (or ρ) are smoothed out on a time scale during which B is correlated but not on the time scale during which P (or ρ) is damped. ρ loses all memory (history) of its past and its future is determined solely by the present on this time scale.[17]

In the last section, we mentioned the Born approximation. This approximation is implemented simply by dropping the $\mathscr{Q}L_{PB}$ term in the exponential operator in K. The resulting memory kernel is still second order in the interaction L_{PB}. In general, this approximation is adequate for a sufficiently large bath that is weakly coupled to the primary system so that the former's (thermal) equilibrium is hardly disturbed by the latter.[3]

We now turn to the sudden approximation. We mentioned earlier the approximation can be applied in two different situations: either the bath or the primary system has the slow coordinates. These two cases are discussed separately as follows.

A. Slow bath–fast primary system

This type of bath has coordinates which do not change much during the time the bath is coupled to the primary system. A bath of this nature is referred to as a slow bath for obvious reasons.[10] (In Sec. V, examples of a slow bath will be given and briefly discussed.)

Since the bath coordinates are slow, the commutator of the (unperturbed) Hamiltonian of B and the interaction between P and B is small,[8–10,13]

$$[H_B,V_{PB}]\simeq 0. \tag{2.16}$$

This in turn implies

$$[L_B,L_{PB}]\simeq 0. \tag{2.17}$$

Using this, the commutation relation

$$[L_B,L_P+\mathscr{Q}L_{PB}]\simeq 0 \tag{2.18}$$

can be easily established. To see the validity of the relation, we notice that L_B commutes with L_P since they are operators in different spaces and because of Eq. (2.17),

$$\begin{aligned}[L_B,\mathscr{Q}L_{PB}]&\simeq-[L_B,\mathscr{P}L_{PB}]=\mathscr{P}L_{PB}\,L_B-L_B\,\mathscr{P}L_{PB}\\&\simeq\mathscr{P}L_B\,L_{PB}-L_B\,\mathscr{P}L_{PB}\end{aligned} \tag{2.19}$$

which vanishes because of Eqs. (2.6) and (2.8). *Notice that the choice of the equilibrium density operator of B for* $B_{\rm ref}$ *in the definition of* $\mathscr{P}$ *[in Eq. (1.2)] is crucial in establishing the commutation relation (2.18).*

From Eq. (2.18), we have

$$\begin{aligned}&\exp[-i(L_B+L_P+\mathscr{Q}L_{PB})t\,]\\&\quad\simeq\exp(-iL_B\,t)\exp[-i(L_P+\mathscr{Q}L_{PB})t\,].\end{aligned} \tag{2.20}$$

Using this and Eq. (2.17), the memory kernel [Eq. (2.10)] becomes

$$\begin{aligned}K(t,t')\simeq&-{\rm Tr}_B\exp[-iL_B(t-t')]L_{PB}\\&\times\exp[-i(L_P+\mathscr{Q}L_{PB})(t-t')]\mathscr{Q}L_{PB}\,\rho_B.\end{aligned} \tag{2.21}$$

When $\exp[-iL_B(t-t')]$ is expanded in a Taylor series

and Eq. (2.6) is used, the memory kernel in the sudden limit becomes

$$K_S(t,t') = -\mathrm{Tr}_B\, L_{PB} \exp[-i(L_P + \mathcal{Q}L_{PB})(t-t')]\mathcal{Q}L_{PB}\rho_B. \quad (2.22)$$

Similarly, the inhomogeneity $I(t)$ [Eq. (2.11)] in the sudden limit is of the form

$$I_S(t) = -i\,\mathrm{Tr}_B\, L_{PB} \exp[-i(L_P + \mathcal{Q}L_{PB})t]\mathcal{Q}W(0). \quad (2.23)$$

The form of the operator L_{eff} in Eq. (1.3) remains the same [Eq. (2.9)] in the sudden limit. This completes our derivation of the sudden GME for a slow bath.

This sudden GME, which involves a non-Markovian memory kernel, is expected to be applicable for those primary systems coupled to baths whose coordinates do not change much during the primary system-bath interaction. Notice that the (unperturbed) bath Liouvillian L_B *is not* present in the propagator $\exp[-i(L_P + \mathcal{Q}L_{PB})\tau]$ appearing in the memory kernel and the inhomogeneity. This is not surprising since the coordinates of the "slow" bath do not change much during the interaction, so the free motion of the bath would not be expected to be important. Hence, under this slow bath condition, L_B is eliminated from the propagator. The resulting GME, however, still has memory effects. Thus in this respect, the sudden approximation is *different* from the Markovian approximation in which *no* memory effects are included. We return to this in Sec. IV when we examine the behavior of the bath correlation functions for a specific model in this approximation.

B. Slow primary system–fast bath

This situation is the opposite of the one considered in the last subsection. Here, the commutator of the (unperturbed) Hamiltonian of P and the interaction is small

$$[H_P, V_{PB}] \simeq 0. \quad (2.24)$$

This in turn implies

$$[L_P, L_{PB}] \simeq 0. \quad (2.25)$$

Using this and Eq. (2.7), we have

$$[L_P, L_B + \mathcal{Q}L_{PB}] \simeq 0. \quad (2.26)$$

Using a relation analogous to Eq. (2.20) with the roles of L_P and L_B being interchanged, we have, under the condition of slow primary system coordinates,

$$K(t,t') \simeq -\mathrm{Tr}_B \exp[-iL_P(t-t')]L_{PB} \times \exp[-i(L_B + \mathcal{Q}L_{PB})(t-t')]\mathcal{Q}L_{PB}\rho_B. \quad (2.27)$$

In the sudden approximation, the Hamiltonian of the slow coordinates is effectively a constant.[13] This holds exactly when the Hamiltonian commutes with the interaction potential. Using this, H_P is approximated by a constant E and for any arbitrary operator X,

$$\exp(-L_P\tau)X = \exp(-i/\hbar H_P\tau)X\exp(-/\hbar H_P\tau) \simeq \exp(-i/\hbar E\tau)X\exp(i/\hbar E\tau) = X. \quad (2.28)$$

Hence, in the sudden limit, the memory kernel and the inhomogeneity are, respectively, in the form

$$K_S(t,t') = -\mathrm{Tr}_B\, L_{PB} \exp[-i(L_B + \mathcal{Q}L_{PB})(t-t')]\mathcal{Q}L_{PB}\rho_B, \quad (2.29)$$

$$I_S(t) = -i\,\mathrm{Tr}_B\, L_{PB} \exp[-i(L_B + \mathcal{Q}L_{PB})t]\mathcal{Q}W(0). \quad (2.30)$$

Notice that, Eqs. (2.29) and (2.30)/(2.22) and (2.23) can be obtained directly by replacing H_P/H_B with a constant without using the commutation conditions (2.26)/(2.18). The former approach is used in order to make the treatment in this and the next section more unified.

The discussions in the last subsection can also be applied here with the role of B being replaced by P, but there is a major difference. Here, the non-Markovian form of the memory kernel in the sudden GME for the slow reduced density operator of the primary system can be further reduced to the Markovian form. In accordance with the assumption of a fast bath and a slow primary system, the bath relaxes on the time scale τ_B, which is much shorter than that of the primary system (or ρ). For $t \gg \tau_B$, we can use the Markovian approximation to simplify the memory kernel (which relaxes on the same scale as τ_B). In particular, for a weak interaction L_{PB} (for which the Born approximation is adequate) and for $\mathcal{P}L_{PB}\mathcal{P}X = 0$ [condition (2.12)], the Markovian-sudden GME for the reduced density operator of a slow primary system is in the form

$$\frac{\partial\rho}{\partial t} = -iL_P\rho - \mathrm{Tr}_B\, L_{PB}\int_0^\infty dt' \times \exp(-iL_B t')L_{PB}\rho_B\rho(t). \quad (2.31)$$

The Markovian-sudden GME of Eq. (2.31) is identical to the (Markovian) GME obtained by the adiabatic elimination method.[11] Apart from using the same projection operator (which has the properties of Eqs. [(2.6)–(2.8) and (2.12)], the two procedures are practically independent. In the latter, two different time scales, fast and slow, are utilized explicitly at a very early stage of the derivation and the fast bath coordinates are "eliminated" using the projection operator. Thus, it is not surprising that the two procedures result in the same GME. For details on the adiabatic elimination method, the reader is referred to Refs. 11 and 12.

III. SUDDEN REPRESENTATION GME

In this section, we derive an *exact* GME which has a form such that when the memory kernel and the inhomogeneity are expanded in a perturbation series, the zeroth order GME is in the sudden approximation form. We will concentrate on the case which has the slow bath and fast primary system coordinates. The other case (with the slow primary system and fast bath coordinates) can be treated analogously.

We first rewrite the evolution operator $\exp(-iLt)$ (for the density operator) using the sudden representation developed recently by Chang *et al.*[13] for the evolution operator $\exp(-i/\hbar Ht)$ (for the wave function) in scattering problems. In this representation, the wave function evolution operator $\exp(-i/\hbar Ht)$ is transformed into a frame that moves synch-

ronously with the motion of the designated slow coordinates which, in our case, are the bath coordinates. The operator in this interaction picture is transformed into the final form[13]

$$\exp(-i/\hbar Ht) = \exp(-i/\hbar H_B\, t) \times \exp[-i/\hbar(H_P + V_{PB})t\,]\, U(t), \tag{3.1}$$

where

$$U(t) = T\exp\left[-i/\hbar \int_0^t dt'\, V_{II}(t')\right], \tag{3.2}$$

$$V_{II}(t) = \exp[i/\hbar(H_P + V_{PB})t\,]\, V_\epsilon(t) \times \exp[-i/\hbar(H_P + V_{PB})t\,], \tag{3.3}$$

$$V_\epsilon(t) = \exp(i/\hbar H_B\, t) V_{PB} \exp(-i/\hbar H_B\, t) - V_{PB}, \tag{3.4}$$

and T is the time ordering operator.

Let $\epsilon = [H_B, V_{PB}]$ and the operator $V_\epsilon(t)$ be written in the form[10,13]

$$\begin{aligned} V_\epsilon(t) &= (V_{PB} + i/\hbar[H_B, V_{PB}]t \\ &\quad + (1/2!)(i/\hbar)^2[H_B,[H_B, V_{PB}]]t^2 + \cdots) - V_{PB} \\ &= i/\hbar\epsilon t + (1/2!)(i/\hbar)^2[H_B,\epsilon]t^2 + \cdots. \end{aligned} \tag{3.5}$$

The parameter ϵ [or $V_\epsilon(t)$] essentially measures the degree of suddenness of the system. In the extreme sudden limit (i.e., $\epsilon = 0$), $V_\epsilon(t)$ and $V_{II}(t)$ vanish and $U(t)$ is just the identity operator. The exponential operator $U(t)$ in Eq. (3.1) can be formally expanded in a Maclaurin series[10] and the zeroth order term of the resulting expression for $\exp(-i/\hbar Ht)$ is just in the sudden approximation form. Because of Eq. (3.5), this series expansion can be regarded as an expansion in terms of the operator ϵ, which is a fundamental parameter of the sudden approximation.[10] Another important feature of the expansion is that the perturbation $V_{II}(t)$ is bounded for all V.[13] For more discussion of the perturbation expansion of $\exp(-i/\hbar Ht)$, the reader is referred to Refs. 10 and 13. In the latter, the expansion is discussed from the path-integral[18] perspective. Using the sudden representation of Eq. (3.1), the operator $\exp(-iLt)$ can be written in the analogous factorized form

$$\exp(-iLt) = \exp(-iL_B\, t)\exp(-iL'\,t)T \times \exp\left[-i\int_0^t dt'\, L_{II}(t')\right], \tag{3.6}$$

where

$$L' = L_P + L_{PB}, \tag{3.7}$$

and L_{II} is the corresponding Liouvillian of V_{II} in Eq. (3.3).

Next, we use the identity (2.5) with L being replaced by L' and proceed as in the case of the Schrödinger representation (discussed in the last section) to write

$$\begin{aligned} \frac{\partial\rho}{\partial t} &= -i\,\mathrm{Tr}_B\, L\exp(-iL_B\, t)\mathscr{P}\exp(-iL'\,t)T\exp\left[-i\int_0^t dt'\, L_{II}(t')\right]W(0) \\ &\quad - \mathrm{Tr}_B\, L\exp(-iL_B\, t)\left[\int_0^t dt'\exp[-i\mathscr{Q}L'(t-t')]\mathscr{Q}L'\mathscr{P}\exp(-iL'\,t')\right]T\exp\left[-i\int_0^t dt'\, L_{II}(t')\right]W(0) \\ &\quad - i\,\mathrm{Tr}_B\, L\exp(-iL_B\, t)\exp(-i\mathscr{Q}L'\,t)\mathscr{Q}T\exp\left[-i\int_0^t dt'\, L_{II}(t')\right]W(0). \end{aligned} \tag{3.8}$$

The first term on the right-hand side of the above equation can be written in a more recognizable form of $-i\,\mathrm{Tr}_B\, L\rho_B\,\rho(t)[\,= -iL_{\mathrm{eff}}\,\rho(t)]$. This can be readily seen using Eqs. (2.6) and (2.8) and the factorized form of the evolution operator in Eq. (3.6). Although, the second and the third term of Eq. (3.8) cannot be identified individually as the memory term and the inhomogeneity of the usual GME, together they must play the same role because Eq. (3.8) is *exact*. In the sudden limit

$$T\exp\left[-i\int_0^t dt'\, L_{II}(t')\right] = 1. \tag{3.9}$$

From this and Eqs. (2.6) and (2.8), it can be shown easily that Eq. (3.8) reduces to the sudden GME with the second and the third term reduced, respectively, to the memory term and the inhomogeneity in the sudden approximation.

Although Eq. (3.8) is a perfectly valid equation of motion for ρ, it suffers from the fact that it is not a GME (in the usual sense). To arrive at this equation, the identity (2.5) was used to decompose the evolution operator of the primary system in the presence of the interaction. In order to obtain the GME, the evolution operator of the former *and* the correction (for separating the unperturbed motion of the bath) have to be decomposed as well. To do this, we just recast the (Schrödinger) evolution operator $\exp(-iLt)$ into a form of *two* factors instead of three as in Eq. (3.6). That is, the factorization of $\exp(-iLt)$ is stopped at the (first) interaction picture stage [by removing $\exp(-iL_B\, t)$ from the density operator W] of the procedure of Chang *et al.*[13] The equation of motion for the density operator $W_I(t)[\,= \exp(iL_B\, t)W(t)]$ in this interaction picture is

$$\frac{\partial W_I}{\partial t} = -i[L' + L_I(t)]W_I, \tag{3.10}$$

where

$$\begin{aligned} L_I(t) &= \exp(iL_B\, t)L_{PB}\exp(-iL_B\, t) - L_{PB} \\ &= [V_\epsilon(t),]. \end{aligned} \tag{3.11}$$

Using the formal solution of Eq. (3.10), the equation of motion for W becomes

$$\frac{\partial W}{\partial t} = -iL\exp(-iL_B\, t)T \times \exp\left\{-i\int_0^t dt'[L' + L_I(t')]\right\}W(0). \tag{3.12}$$

The analogous identity (2.5) for

$$T\exp\left\{-i\int_0^t dt'[L' + L_I(t')]\right\} \text{ is}$$

$$T\exp\left\{-i\int_0^t dt'[L'+L_I(t')]\right\}$$
$$=\mathscr{P}T\exp\left\{-i\int_0^t dt'[L'+L_I(t')]\right\}$$
$$-\int_0^t dt'\,T\exp\left\{-i\int_{t'}^t dt''\,\mathscr{Q}[L'+L_I(t'')]\right\}$$
$$\times\mathscr{Q}i[L'+L_I(t')]\mathscr{P}T$$
$$\times\exp\left\{-i\int_0^{t'} dt''[L'+L_I(t'')]\right\}$$
$$+T\exp\left\{-i\int_0^t dt'\,\mathscr{Q}[L'+L_I(t')]\right\}\mathscr{Q}. \quad (3.13)$$

It should be clear by now, using the above identity, that an alternative exact GME can be derived. The operator L_{eff} is again given by Eq. (2.9) and the memory kernel and the inhomogeneity are given by

$$K(t,t') = -\mathrm{Tr}_B\,L\exp(-iL_B\,t)T$$
$$\times\exp\left\{-i\int_{t'}^t dt''\,\mathscr{Q}[L'+L_I(t'')]\right\}$$
$$\times\mathscr{Q}[L'+L_I(t')]\rho_B, \quad (3.14)$$
$$I(t) = -i\,\mathrm{Tr}_B\,L\exp(-iL_B\,t)T$$
$$\times\exp\left\{-i\int_0^t dt'\,\mathscr{Q}[L'+L_I(t')]\right\}\mathscr{Q}W(0). \quad (3.15)$$

Here, Eq. (2.6) has been used explicitly in Eq. (3.14). In the sudden limit, $L_I(t)\equiv 0$, K and I reduce to the sudden approximation form K_S [Eq. (2.22)] and I_S [Eq. (2.23)], respectively. This alternative (exact) GME will be referred to as the sudden representation GME.

The expressions Eqs. (3.14) and (3.15) for the memory kernel and the inhomogeneity are rather complicated. Nevertheless, the exponential operator $T\exp\{-i\int_{t'}^t dt''\,\mathscr{Q}[L'+L_I(t'')]\}$ in these expressions can be expanded formally in terms of $L_I(t'')$ which essentially measures the suddenness of the bath [see the discussion following Eq. (3.5)]. The formal expansion of $T\exp[-i\int_0^t dt'\,L_{II}(t')]$ in Eq. (3.8) in terms of $L_{II}(t')$ is far simpler in this respect even though Eq. (3.8) suffers from not being a GME. The sudden representation GME with its perturbation expansion might be useful for a bath with an appreciable degree of suddenness.

Similar GME's can be derived for the case involving the fast bath and slow primary system coordinates in the sudden limit. Here, the unperturbed motion of the primary system is removed instead in forming the interaction picture. In this case, the memory kernel of the resulting GME is given by

$$K(t,t') = -\mathrm{Tr}_B\,L\exp(-iL_P\,t)T$$
$$\times\exp\left\{-i\int_{t'}^t dt''\,\mathscr{Q}[L'+L_I(t'')]\right\}$$
$$\times\mathscr{Q}[L'+L_I(t')]\exp(iL_P\,t')\rho_B, \quad (3.16)$$

where $L'=L_B+L_{PB}$ and $L_I(t')$ is given by an expression analogous to Eq. (3.11) with L_B replaced by L_P. Here, Eq. (2.7) has been used explicitly. Compared to Eq. (3.14), there is an extra operator between $\mathscr{Q}[L'+L_I(t')]$ and ρ_B in Eq. (3.16). This is because $\mathscr{P}L_P\,X=L_P\,\mathscr{P}X\neq 0$ in contrast to $\mathscr{P}L_B\,X=L_B\,\mathscr{P}X=0$ in the previous case. The inhomogeneity I is given by an analogous expression of Eq. (3.15) with the appropriate modifications.

IV. THE DAMPED HARMONIC OSCILLATOR

In this section, we consider a harmonic oscillator coupled to a heat bath. This elementary system is used frequently in modeling quantum optical processes and its treatment has been covered extensively in the literature.[3,4,17,19] Here, we only use this simple system to illustrate and discuss the form of the different GME's considered in this paper. Questions concerning the nature of the solutions of the GME's will not be discussed here.

The Hamiltonian of the harmonic oscillator (our primary system) is in the form

$$H_P=\hbar\omega(a^\dagger a+1/2), \quad (4.1)$$

where $a^\dagger$ and a are the creation and annihilation Bose operators and ω is the natural frequency of the oscillator. For simplicity, we also assume that the heat bath is made up of a large number of independent harmonic oscillators with (Bose) operators $b_i^\dagger$ and b_i and frequencies ω_i and

$$H_B=\hbar\sum_i\omega_i(b_i^\dagger b_i+1/2). \quad (4.2)$$

The coupling between P and B can be chosen to be[4,11,17]

$$V_{PB}=\hbar\sum_i(g_i\,ab_i^\dagger+g_i^*\,a^\dagger b_i), \quad (4.3)$$

where the coupling constants g_i can be functions of time. In this model, we have

$$\mathrm{Tr}_B\,\rho_B\,b_i^\dagger=\mathrm{Tr}_B\,\rho_B\,b_i=0. \quad (4.4)$$

Hence, condition $\mathscr{P}L_{PB}\,\mathscr{P}X=0$ (2.12) for the projection operator is automatically satisfied. From now on, the oscillator comprising P will be referred to as the primary oscillator. In the following treatment, the heat bath is assumed to have certain properties. It is in thermal equilibrium before being coupled to the primary oscillator and it is sufficiently large and weakly coupled to the latter that its equilibrium is hardly disturbed. The first condition implies the inhomogeneity term in the GME vanishes and the second condition ensures that the Born approximation is adequate in describing the dynamics of the system. The heat bath may be required to have additional properties when a different GME is considered.

The Born approximation GME for the reduced density operator of the primary oscillator is

$$\frac{\partial\rho}{\partial t}=-iL_P\,\rho(t)-\int_0^t d\tau\,\mathrm{Tr}_B\,L_{PB}\exp[-i(L_P+L_B)\tau]L_{PB}\,\rho_B\,\rho(t-\tau)=-i/\hbar[H_P,\rho(t)]$$
$$-\left(\frac{1}{\hbar}\right)^2\int_0^t d\tau\,\mathrm{Tr}_B\left([V_{PB},\exp[-i/\hbar(H_P+H_B)\tau][V_{PB},\rho_B\,\rho(t-\tau)]\exp[i/\hbar(H_P+H_B)\tau]\right). \quad (4.5)$$

Let $\langle X \rangle = \mathrm{Tr}_B \rho_B X$,

$$b_i(t) = \exp(i/\hbar H_B t) b_i \exp(-i/\hbar H_B t), \tag{4.6}$$

and

$$\mathcal{A}(t) = \sum_i g_i^* b_i(t). \tag{4.7}$$

Using Eqs. (4.1)–(4.3) and (4.6)–(4.7) and the fact that

$$\langle b_i^\dagger b_j^\dagger \rangle = \langle b_i b_j \rangle = 0, \text{ for any } i, j, \tag{4.8}$$

Eq. (4.5) becomes

$$\begin{aligned}\frac{\partial \rho}{\partial t} = & -i\omega[a^\dagger a, \rho(t)] \\ & + \int_0^t d\tau \{ \langle \mathcal{A}^\dagger \mathcal{A}(\tau) \rangle e^{i\omega\tau} [a^\dagger \tilde{\rho}(t-\tau) a - \tilde{\rho}(t-\tau) a a^\dagger] \\ & + \langle \mathcal{A}(\tau) \mathcal{A}^\dagger \rangle e^{i\omega\tau} [a \tilde{\rho}(t-\tau) a^\dagger - a^\dagger a \tilde{\rho}(t-\tau)] \\ & + \langle \mathcal{A}^\dagger(\tau) \mathcal{A} \rangle e^{-i\omega\tau} [a^\dagger \tilde{\rho}(t-\tau) a - a a^\dagger \tilde{\rho}(t-\tau)] \\ & + \langle \mathcal{A} \mathcal{A}^\dagger(\tau) \rangle e^{-i\omega\tau} [a \tilde{\rho}(t-\tau) a^\dagger - \tilde{\rho}(t-\tau) a^\dagger a] \}, \end{aligned} \tag{4.9}$$

where

$$\tilde{\rho}(t-\tau) = e^{-i/\hbar H_P \tau} \rho(t-\tau) e^{i/\hbar H_P \tau} = e^{-iL_P \tau} \rho(t-\tau). \tag{4.10}$$

The third and the fourth terms inside the curly bracket are, respectively, the Hermitian conjugates of the first and second terms. The influence of the heat bath on the primary oscillator is through the bath correlation functions $\langle \mathcal{A}^\dagger \mathcal{A}(\tau) \rangle$, $\langle \mathcal{A}(\tau) \mathcal{A}^\dagger \rangle$, etc. which can be evaluated explicitly using the form of H_B in Eq. (4.2).

We now consider the Markovian approximation which is adequate when the bath relaxes much faster than the primary oscillator. The usual treatment is to transform Eq. (4.9) to the interaction picture (IP).[20] The equation of motion for the IP reduced density operator $\rho^I(t) [= e^{iL_P t} \rho(t)]$ is given by an equation analogous to Eq. (4.9) without the first term on the right-hand side and with ρ and $\tilde{\rho}$ replaced by ρ^I. Under the Markovian condition, the bath correlation functions decay much faster than $\rho^I(t-\tau)$ does. The latter can be replaced by $\rho^I(t)$. *This is equivalent to approximating $\tilde{\rho}(t-\tau)$ in Eq. (4.9) [Eq. (4.10)] by $\rho(t)$.* The upper limit of the integral in the equation of motion for ρ^I or ρ can be extended to infinity. Following the treatment of Haake,[3] three real parameters κ, Δ, and $\bar{n}$, used commonly in quantum optics, are defined in terms of the bath correlation functions such that

$$\kappa + i\Delta = \int_0^\infty d\tau\, e^{i\omega\tau} \langle [\mathcal{A}(\tau), \mathcal{A}^\dagger] \rangle, \tag{4.11}$$

$$\kappa \bar{n} = \mathrm{Re} \int_0^\infty d\tau\, e^{i\omega\tau} \langle \mathcal{A}^\dagger \mathcal{A}(\tau) \rangle. \tag{4.12}$$

The influence of the heat bath on the primary oscillator is characterized by these parameters and the resulting (Born approximation) Markovian GME in the Schrödinger picture is given by[3,17]

$$\begin{aligned}\frac{\partial \rho}{\partial t} = & -i(\omega + \Delta)[a^\dagger a, \rho] + \kappa \{ [a, \rho a^\dagger] \\ & + [a\rho, a^\dagger] \} + 2\kappa\bar{n} [a, [\rho, a^\dagger]]. \end{aligned} \tag{4.13}$$

The parameter Δ represents the frequency shift of the primary oscillator. κ is the damping constant and the second term of the equation represents the energy loss from the oscillator to the heat bath. The last term of the equation is the thermal noise and

$$\bar{n} = (e^{\beta\hbar\omega} - 1)^{-1} \tag{4.14}$$

is the mean occupation number of the primary oscillator for thermal equilibrium at temperature $T = [1/(k_B \beta)]$. When $T \to 0$, $\bar{n} \to 0$ in Eq. (4.14). This can also be seen from Eq. (4.12). Under this condition $\rho_B = |0\rangle\langle 0|(|0\rangle$: the vacuum state of the bath oscillators) and all $\langle b_i^\dagger b_i(\tau) \rangle$ vanish. (At other temperatures T, $\langle b_i^\dagger b_j(\tau) \rangle \propto \delta_{ij}$ since the bath oscillators are independent of each other.) For detailed discussions of Eq. (4.13) and the discussions on the corresponding Fokker–Planck equation for the associated distribution function of ρ, the reader is referred to Refs. 3 and 17.

We now consider the sudden GME. First, we consider the case of a slow bath and a fast primary oscillator. The corresponding (Born approximation) GME is given by an equation analogous to Eq. (4.9) but now *the bath correlation functions no longer depend on time because the bath Liouvillian is not present in the memory kernel.* The reduction of Eq. (4.9) or the exact GME to the sudden approximation form is straightforward. For a slow bath, each bath oscillator vibrates at a very low frequency ω_i and in the limit $\omega_i \to 0$,[10] $b_i(t) \to b_i$ in Eq. (4.6) and $\mathcal{A}(t) \to \mathcal{A}$ in Eq. (4.9) and the sudden GME (for a slow bath) is recovered.

In contrast to the Markovian approximation for a fast bath, the bath correlation functions in the sudden approximation for a slow bath behave like a fairly "flat" or approximately constant function of time instead of the delta function-like behavior. Hence, the slow bath has a very long range memory effect on the primary oscillator. The two approximations are exactly opposite in this respect.

In the above analysis, we implicitly assumed the coupling constants g_i [in Eq. (4.3)] are independent of time. When the g_i are functions of time, they can be factored out of the correlation functions and the same analysis again follows.

The GME for a fast bath and a slow primary oscillator can be treated similarly. The sudden GME is given by an equation analogous to Eq. (4.9) with $\tilde{\rho}$ replaced by ρ and $\exp(\pm i\omega\tau)$ by the identity operator. The Markovian-sudden GME of Eq. (2.31) has the same form of Eq. (4.13) with the parameters κ, Δ, and $\bar{n}$ defined via[11]

$$\kappa + i\Delta = \int_0^\infty d\tau \langle [\mathcal{A}(\tau), \mathcal{A}^\dagger] \rangle \tag{4.15}$$

and

$$\kappa \bar{n} = \mathrm{Re} \int_0^\infty d\tau \langle \mathcal{A}^\dagger \mathcal{A}(\tau) \rangle \tag{4.16}$$

and $\bar{n}$ is again given by Eq. (4.14). The three parameters have the same physical interpretation as before. The transition from Eqs. (4.11) and (4.12) to Eqs. (4.15) and (4.16) is obvious by now. In the slow primary oscillator limit, $\omega \to 0$ and Eqs. (4.11) and (4.12) reduce to Eqs. (4.15) and (4.16), respectively.

Finally, we conclude this section with some remarks. First, it is not necessary to use harmonic oscillators as the bath system. Any unspecified heat bath Hamiltonian H_B

with dimensionless bath operators $b_i^\dagger$ and b_i can be used as well.[3] In this case, Eq. (4.4) is no longer satisfied in general. Since the mean conservative force exerted on the primary oscillator by the heat bath does not affect the damping (or dissipation) of the former, Eq. (4.4) and $\mathscr{P}L_{PB}\,\mathscr{P}X = 0$ can be assumed to hold. Also in this general case, Eq. (4.8) no longer holds and there should be four more terms involving $\langle \mathscr{A}^\dagger \mathscr{A}^\dagger(\tau)\rangle$ and $\langle \mathscr{A}(\tau)\mathscr{A}\rangle$ and the corresponding Hermitian conjugates in Eq. (4.9). Each of these extra terms is associated with a factor involving either two a's or two $a^\dagger$'s. These factors represent nonresonant processes which are usually ignored in the rotating wave approximation used commonly in quantum optics.[19–21] Second, the treatment of the damped oscillator can be adapted easily to treat spin relaxation processes[5,22] and to describe spontaneous emission of electromagnetic radiation by an initially excited two-level atom.[20] In the former H_B is the "lattice" Hamiltonian which describes the translational, vibrational and rotational motion of the molecule and H_{PB} is the coupling of the spin to the surroundings (i.e., the other motions of the molecule). The slow bath can be used to describe some of the molecular degrees of freedom. In the two-level atom system, the electromagnetic field is treated as the bath into which the atom dissipates its excitation energy.

V. DISCUSSION

In this paper, we have examined the GME using the sudden approximation. Although the approximation has been hinted at earlier[23] (in an entirely different fashion), we believe this is the first systematic study of sudden approximation GME's. The sudden representation GME, in spite of its rather involved and complicated form, opens a new way in developing approximation schemes based on perturbation expansions.

Recently, stochastic methods, based on the master, the Langevin or the Fokker–Planck equations, have been used in studying scattering problems.[24] The sudden GME may be useful for studying multiple time scale collision systems. For instance, consider a molecule–surface collision system. When a gaseous particle hits and scatters quickly from a surface composed of very massive particles, each lattice point of the surface should not deviate much from its equilibrium position. The surface (except the part being struck) can be treated as a slow bath and the sudden GME (for a slow bath) could be useful in studying the energy transfer between the projectile and the surface. Another example would be gas phase collisions of molecules with lots of internal degrees of freedom. Since the vibrational motions are generally much faster than the rotational motions, the latter can be treated as slow compared to the former. The sudden GME's for the slow bath and the fast bath can be used to study the vibrational and rotational transitions, respectively.

We point out that our analysis has been on a composite system $(P + B)$ with the (total) Liouvillian given by Eq. (2.2). Our analysis can be extended easily to a more general system in which $P + B$ may be an open system moving irreversibly under the influence of another larger system C characterized by relaxation times much shorter than those of $P + B$.[3,4,25] It can also be applied to a system in the presence of external classical fields (perturbations).[3,4,25] In this general system, the Liouvillian will be in the form $L_P + i\Lambda_P + L_B + i\Lambda_B + L_{PB} + L_{\rm ext}(t)$, where Λ_P, Λ_B are the dissipative terms due to C and $L_{\rm ext}$ is the external field acting on $P + B$.

Finally, we also point out our analysis is based on the GME's resulting from using the form of the projection operators of Eq. (1.2). Currently, we are extending the analysis using other more general projection operators.[14,26,27] The possibility of using the sudden approximation for generalized Langevin[15,28] and generalized Fokker–Planck equations[11,14,29] is also being considered.

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