Journal of Statistical Physics, Vol. 17, No. 4, 1977

A Generalized Stochastic Liouville Equation. Non-Markovian Versus Memoryless Master Equations

Fumiaki Shibata,[1] Yoshinori Takahashi,[2] and Natsuki Hashitsume[1]

Received November 23, 1976; revised March 4, 1977

The interrelation between the well-known non-Markovian master equation and the new memoryless one used in the previous paper is clarified on the basis of damping theory. The latter equation is generalized to include cases in which the Hamiltonian or the Liouvillian is a random function of time, and is written in a form feasible for perturbational analysis. Thus, the existing stochastic theory in which those cases mentioned above are discussed is equipped with a more tractable basic equation. Two problems discussed in the previous paper, i.e., the random frequency modulation of a quantal oscillator and the Brownian motion of a spin, are treated from the viewpoint of the stochastic theory without such explicit consideration of external reservoirs as was taken in the previous paper.

KEY WORDS: Statistical mechanics; damping theory; master equation; Brownian motion; quantal oscillator; spin.

1. INTRODUCTION

Damping theory was long known as involving a *non-Markovian* master equation.[(1)] The memory term in this equation was of great interest, and it was believed that the memory effect would be inevitable, until Tokuyama and Mori[(2)] showed the possibility of a *memoryless* master equation[3] by a very complicated and seemingly arbitrary manipulation. It was desired to simplify the method of derivation of the Tokuyama–Mori equation and also to clarify the interrelationship between the latter equation and damping theory.

In a previous paper,[(4)] we succeeded in deriving by a very simple method a new expression for a memoryless master equation, which was shown to be

[1] Department of Physics, Faculty of Science, Ochanomizu University, Tokyo, Japan.
[2] Department of Physics, Faculty of Science, University of Tokyo, Tokyo, Japan.
[3] See Refs. 3 for earlier references on this subject.

equivalent to the Tokuyama–Mori equation. As was mentioned in that paper, this method of derivation should be intimately related to damping theory. The first aim of the present paper is to give the derivation concerned in such a way as to show that the new memoryless equation is in fact an improved solution of the damping theory, or, in other words, is obtained as the result of a *renormalization of the memory effect.*

Although in that paper the new master equation was successfully applied to two examples of a system in contact with a heat reservoir, i.e., the Brownian motion of a quantal oscillator and that of a spin, it is more convenient in practical applications to introduce random forces acting upon a system than to consider explicit interactions with a reservoir. This is the well-known method of the *stochastic Liouville equation* formulated by Kubo and applied by him in the stochastic theory of the spectral line shape.(5) If our method of deriving the memoryless master equation could be generalized so as to be applicable to a system having a stochastic or *time-dependent Hamiltonian*, the whole wealth of the stochastic theory of the line shape would be attained on the basis of a more tractable and powerful memoryless master equation. This generalization is the second aim of the present paper.

In Section 2 we consider a system having a *time-independent* Hamiltonian to show our damping-theoretical derivation of the memoryless master equation mentioned above. In Section 3 this method of derivation is generalized for a system represented by a stochastic Hamiltonian. As was done in the previous paper, the transformation of our generalized memoryless equation into the form useful for perturbational expansion is also done in this section. The resulting expression is slightly complicated compared with that given in the previous paper because of the appearance of ordered exponentials. In Section 4 our master equation is applied to the stochastic versions of two examples discussed in the previous paper, i.e., the Brownian motion of a quantal oscillator and that of a spin. As in the previous paper, the transcription into the phase-space c-number language is performed for these examples, and the resulting equations are compared with those given in the Kubo line shape theory. Finally, in Section 5 we give a few remarks. We use units where $\hbar = 1$.

2. THE DAMPING-THEORETICAL DERIVATION OF THE MEMORYLESS EQUATION OF MOTION FOR A REDUCED DENSITY MATRIX

Let us consider a system having a *time-independent* Hamiltonian $\mathscr{H}$. Its time evolution is governed by the quantal Liouville equation

$$\dot{W}(t) = -i[\mathscr{H}, W(t)] \equiv -iLW(t) \tag{1}$$

where L denotes the Liouvillian corresponding to $\mathscr{H}$, and $W(t)$ is the density matrix of the system. Irrelevant information about the system is eliminated by virtue of a *time-independent* projection operator $\mathscr{P}$, and relevant information is assumed to be given by the projected density matrix $\mathscr{P}W(t)$. We want to derive an equation of motion for this $\mathscr{P}W(t)$. This is done by the method of damping theory.

On multiplying Eq. (1) by $\mathscr{P}$ or $\mathscr{Q} = 1 - \mathscr{P}$, we obtain the following coupled equations:

$$\mathscr{P}\dot{W}(t) = -i\mathscr{P}L\mathscr{P}W(t) - i\mathscr{P}L\mathscr{Q}W(t) \tag{2a}$$

$$\mathscr{Q}\dot{W}(t) = -i\mathscr{Q}L\mathscr{P}W(t) - i\mathscr{Q}L\mathscr{Q}W(t) \tag{2b}$$

The second equation (2b) can be integrated to give

$$\mathscr{Q}W(t) = -\int_0^t e^{-i\mathscr{Q}L\tau} i\mathscr{Q}L\mathscr{P}W(t-\tau)\, d\tau + e^{-i\mathscr{Q}Lt}\mathscr{Q}W(0) \tag{3}$$

In the conventional treatment,[1] we insert this expression for $\mathscr{Q}W(t)$ into the last term of Eq. (2a) and obtain the well-known non-Markovian equation

$$\mathscr{P}\dot{W}(t) = -i\mathscr{P}L\mathscr{P}W(t) - \int_0^t \mathscr{P}Le^{-i\mathscr{Q}L\tau}\mathscr{Q}L\mathscr{P}W(t-\tau)\, d\tau$$
$$- i\mathscr{P}Le^{-i\mathscr{Q}Lt}\mathscr{Q}W(0) \tag{4}$$

In order to derive our memoryless equation, we first eliminate the memory in the time-integral term of Eq. (3) by making use of the solution of the original equation (1) in the form

$$W(t-\tau) = e^{iL\tau}W(t) \tag{5}$$

Thus we can reduce Eq. (3) into a memoryless form:

$$\mathscr{Q}W(t) = -\int_0^t e^{-i\mathscr{Q}L\tau} i\mathscr{Q}L\mathscr{P}e^{iL\tau}\, d\tau \cdot (\mathscr{P} + \mathscr{Q})W(t)$$
$$+ e^{-i\mathscr{Q}Lt}\mathscr{Q}W(0) \tag{6}$$

This equation is again an equation for $\mathscr{Q}W(t)$, which we should solve. By this procedure, we perform the renormalization of the memory effect. Collecting terms containing $\mathscr{Q}W(t)$ on the left-hand side, we obtain

$$f(t)\mathscr{Q}W(t) = \{1 - f(t)\}\mathscr{P}W(t) + e^{-i\mathscr{Q}Lt}\mathscr{Q}W(0) \tag{7}$$

where we have defined

$$f(t) = 1 + \int_0^t e^{-i\mathscr{Q}L\tau} i\mathscr{Q}L\mathscr{P}e^{iL\tau}\, d\tau$$
$$= \mathscr{P} + e^{-i\mathscr{Q}Lt}\mathscr{Q}e^{iLt} \tag{8}$$

The last expression for $f(t)$ is nothing else than the one in the previous paper.[4] Introducing the inverse of $f(t)$,

$$\theta(t) = [f(t)]^{-1} \tag{9}$$

we find the new expression for $\mathcal{Q}W(t)$ in terms of $\mathcal{P}W(t)$ and $\mathcal{Q}W(0)$:

$$\mathcal{Q}W(t) = \{\theta(t) - 1\}\mathcal{P}W(t) + \theta(t)e^{-i\mathcal{Q}Lt}\mathcal{Q}W(0) \tag{10}$$

Substituting this expression into Eq. (2a), we obtain our desired equation:

$$\begin{aligned}\mathcal{P}\dot{W}(t) = & -i\mathcal{P}L\mathcal{P}W(t) - i\mathcal{P}L\{\theta(t) - 1\}\mathcal{P}W(t) \\ & - i\mathcal{P}L\theta(t)e^{-i\mathcal{Q}Lt}\mathcal{Q}W(0)\end{aligned} \tag{11}$$

which is the one derived and proved to be equivalent to the Tokuyama–Mori equation in the previous paper.

It should be remarked that, when we use the term "memoryless," we are neglecting in Eq. (11) the last term, which is known as the destruction term because it describes the destruction process of initial irrelevant information contained in $\mathcal{Q}W(0)$. In the following sections we shall assume the usual initial condition

$$\mathcal{Q}W(0) = 0 \tag{12}$$

for simplicity.

3. GENERALIZATION TO STOCHASTIC HAMILTONIAN

As was stated in the introduction, in various applications in physics it is sometimes necessary to incorporate the stochastic nature of a problem into our theory. We can discuss phenomena more easily by regarding interactions of a system with its surroundings as those induced by random forces acting on the system. This approximation leads to a *stochastic Hamiltonian*, which is a random function of time. Thus we assume a Hamiltonian of the form

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t) \tag{13}$$

where $\mathcal{H}_0$ is the Hamiltonian of the system alone and $\mathcal{H}_1(t)$ represents random external perturbations. We do not consider the origin of the randomness, i.e., the motion of the surroundings, explicitly. The true quantal Liouville equation is replaced by a stochastic quantal Liouville equation:

$$\dot{W}(t) = -i[\mathcal{H}_0 + \mathcal{H}_1(t), W(t)] = -iL(t)W(t) \tag{14}$$

where $L(t) = L_0 + L_1(t)$ is the corresponding stochastic Liouvillian. The projection operator $\mathcal{P}$, which eliminates irrelevant information about the surroundings, is now replaced by an average over a stochastic process $\mathcal{H}_1(t)$. We denote this by

$$\mathcal{P}X = \langle X\rangle_B \tag{15}$$

where $\langle\cdots\rangle_B$ represents that average. The idempotent property $\mathscr{P}^2 = \mathscr{P}$ is automatically satisfied by the condition $\langle 1\rangle_B = 1$.

Since the projection operator is *time-independent*, we obtain at once from Eq. (14) the following coupled equations:

$$\mathscr{P}\dot{W}(t) = -i\mathscr{P}L(t)\mathscr{P}W(t) - i\mathscr{P}L(t)\mathscr{Q}W(t) \tag{16a}$$

$$\mathscr{Q}\dot{W}(t) = -i\mathscr{Q}L(t)\mathscr{P}W(t) - i\mathscr{Q}L(t)\mathscr{Q}W(t) \tag{16b}$$

as before. The second equation can be solved by making use of the ordered exponential

$$\mathscr{G}(t, \tau) = \exp_{\leftarrow}\left[-i\mathscr{Q}\int_\tau^t L(s)\, ds\right] \tag{17}$$

where we use the chronological ordering. The solution is

$$\mathscr{Q}W(t) = -\int_0^t \mathscr{G}(t, \tau)i\mathscr{Q}L(\tau)\mathscr{P}W(\tau)\, d\tau + \mathscr{G}(t, 0)\mathscr{Q}W(0) \tag{18}$$

By introducing another ordered exponential

$$G(t, \tau) = \exp_{\rightarrow}\left[i\int_\tau^t L(s)\, ds\right] \tag{19}$$

we can solve Eq. (14) to obtain

$$W(\tau) = G(t, \tau)W(t) \tag{20}$$

Substituting this expression into Eq. (18), we arrive at the equation for $\mathscr{Q}W(t)$:

$$\mathscr{Q}W(t) = -\int_0^t \mathscr{G}(t, \tau)i\mathscr{Q}L(\tau)\mathscr{P}G(t, \tau)\, d\tau\cdot(\mathscr{P} + \mathscr{Q})W(t) + \mathscr{G}(t, 0)\mathscr{Q}W(0)$$

which can be rewritten as before in the form

$$f(t)\mathscr{Q}W(t) = \{1 - f(t)\}\mathscr{P}W(t) + \mathscr{G}(t, 0)\mathscr{Q}W(0)$$

where we have introduced

$$f(t) = 1 + \int_0^t \mathscr{G}(t, \tau)i\mathscr{Q}L(\tau)\mathscr{P}G(t, \tau)\, d\tau \tag{21}$$

Denoting the inverse of $f(t)$ as $\theta(t)$, we obtain

$$\mathscr{Q}W(t) = \{\theta(t) - 1\}\mathscr{P}W(t) + \theta(t)\mathscr{G}(t, 0)\mathscr{Q}W(0)$$

which gives in turn the desired equation

$$\begin{aligned}\mathscr{P}\dot{W}(t) = &-i\mathscr{P}L(t)\mathscr{P}W(t) - i\mathscr{P}L(t)\{\theta(t) - 1\}\mathscr{P}W(t)\\ &- i\mathscr{P}L(t)\theta(t)\mathscr{G}(t, 0)\mathscr{Q}W(0)\end{aligned} \tag{22}$$

This is the generalization of the previous equation (11) for the case of a time-dependent Hamiltonian.

We can easily rewrite Eq. (22) into the form corresponding to that proposed by Tokuyama and Mori in the case of a time-independent Hamiltonian, by making use of the relation

$$\theta(t) - 1 = \int_0^t \dot{\theta}(\tau)\, d\tau = -\int_0^t \theta(\tau)\dot{f}(\tau)\theta(\tau)\, d\tau \tag{23}$$

The resulting expression is

$$\begin{aligned}\mathscr{P}\dot{W}(t) = & -i\mathscr{P}L(t)\mathscr{P}W(t) + \int_0^t i\mathscr{P}L(t)\theta(\tau)\dot{f}(\tau)\theta(\tau)\, d\tau\, \mathscr{P}W(t) \\ & - i\mathscr{P}L(t)\theta(t)\mathscr{G}(t, 0)\mathscr{Q}W(0)\end{aligned} \tag{24}$$

However, it seems that this expression has no particular advantage over the previous one, (22).

Now let us proceed to transform our expression (22) into a form convenient for the perturbational expansion. This transformation can be performed step by step in parallel with that done in the previous paper. First, for the propagator (19) we have

$$G(t, \tau) = U_0(\tau)R(t, \tau)U_0(-t) \tag{25}$$

where $U_0(t)$ denotes the free propagator

$$U_0(t) = e^{-iL_0t} \tag{26}$$

and $R(t, \tau)$ is the propagator in the interaction picture

$$R(t, \tau) = \exp_{\rightarrow}\left[i\int_\tau^t U_0(-s)L_1(-s)U_0(s)\, ds\right] \tag{27}$$

Similarly, for the projected propagator (17) we obtain

$$\mathscr{G}(t, \tau) = V_0(t)S(t, \tau)V_0(-\tau) \tag{28}$$

where we have put

$$V_0(t) = e^{-i\mathscr{Q}L_0\mathscr{Q}t} \tag{29}$$

and

$$S(t, \tau) = \exp_{\leftarrow}\left[-i\int_\tau^t V_0(-s)\mathscr{Q}L_1(s)\mathscr{Q}V_0(s)\, ds\right] \tag{30}$$

Since our projection operator (15) commutes with L_0:

$$\mathscr{P}L_0 = L_0\mathscr{P}, \qquad \text{and thus} \qquad \mathscr{Q}L_0 = L_0\mathscr{Q} \tag{31}$$

the free propagator $U_0(t)$ also commutes with $\mathscr{P}$ and $\mathscr{Q}$, and hence we can write $V_0(t)$ in the form

$$V_0(t) = \mathscr{P} + \mathscr{Q}U_0(t)\mathscr{Q} \tag{32}$$

This gives in turn the expression

$$\begin{aligned}\mathscr{G}(t, \tau)\mathscr{Q} &= \mathscr{Q} \exp_{\leftarrow}\left[-i\int_{\tau}^{t} \mathscr{Q}L(s)\mathscr{Q}\, ds\right] \\ &= \mathscr{Q}U_0(t)S(t, \tau)U_0(-\tau)\end{aligned} \tag{33}$$

The expressions (25) and (33) have already been ordered in the chronological form. Therefore the expression of $S(t, \tau)$ is simplified to

$$S(t, \tau) = \exp_{\leftarrow}\left[-i\int_{\tau}^{t} \mathscr{Q}U_0(-s)L_1(s)U(s)\mathscr{Q}\, ds\right] \tag{34}$$

Thus we arrive at the desired expression for $f(t)$:

$$f(t) = 1 + \Sigma(t) \tag{35}$$

where we have defined

$$\Sigma(t) = \int_0^t U_0(t)S(t, \tau)U_0(-\tau)\mathscr{Q}iL_1(\tau)\mathscr{P}U_0(-t)R(t, \tau)U_0(\tau)\, d\tau \tag{36}$$

Assuming the initial condition (12) and using the explicit notation of the projection operator (15), we obtain for the reduced density matrix

$$\rho(t) = \mathscr{P}W(t) = \langle W(t)\rangle_B \tag{37}$$

the equation

$$\dot{\rho}(t) = -i(L_0 + \langle L_1(t)\rangle_B)\rho(t) - \Psi(t)\rho(t) \tag{38}$$

where we have defined

$$\Psi(t) = \langle iL(t)\{\theta(t) - 1\}\rangle_B = -i\left\langle L(t)\frac{\Sigma(t)}{1 + \Sigma(t)}\right\rangle_B \tag{39}$$

If we retain terms up to $O(L_1^2(t))$ in accord with the assumption of a Gaussian process, we may approximate the operator (39) as

$$\Psi(t) = \int_0^t \langle L_1(t)\mathscr{Q}U_0(\tau)L_1(t - \tau)U_0(-\tau)\rangle_B\, d\tau \tag{40}$$

In the next section we investigate two examples of relaxation phenomena based on this approximation, and show its usefulness.

4. SIMPLE APPLICATIONS

In this section we assume that external random forces vanish on the average:

$$\langle L_1(t)\rangle_B = 0 \tag{41}$$

Then Eq. (38) for the reduced density matrix within the approximation (40) takes the form

$$\dot{\rho}(t) = -iL_0\rho(t) + \left\{\int_0^t \langle [e^{-i\mathscr{H}_0\tau}\mathscr{H}_1(t-\tau)e^{i\mathscr{H}_0\tau}\rho(t), \mathscr{H}_1(t)]\rangle_B \, d\tau + \text{H.c.}\right\} \tag{42}$$

Let us apply this equation to the following two examples.

Example (i). Random Frequency and Amplitude Modulations. A quantal oscillator with modulated frequency and amplitude may be represented by the stochastic Hamiltonian (13), in which

$$\mathscr{H}_0 = \omega_0 b^\dagger b, \qquad \mathscr{H}_1(t) = \omega_1(t)b^\dagger b + g\{B(t)b^\dagger + B^*(t)b\} \tag{43}$$

$\omega_1(t)$ and $B(t)$ are independent, stationary, random c-number functions of time. g is a coupling constant. Obviously, Eq. (42) becomes

$$\begin{aligned}\dot{\rho}(t) = &-i\omega_0[b^\dagger b, \rho(t)] + \{\tfrac{1}{2}\dot{C}(t)[b^\dagger b\rho(t), b^\dagger b] \\ &+ \phi(t)[b^\dagger\rho(t), b] + \phi^*(t)[b\rho(t), b^\dagger] + \text{H.c.}\}\end{aligned} \tag{44}$$

where the following functions are defined:

$$C(t) = 2\int_0^t (t-\tau)\langle\omega_1(\tau)\omega_1(0)\rangle_B \, d\tau \tag{45a}$$

$$\phi(t) = g^2\int_0^t \langle B^*(\tau)B(0)\rangle e^{-i\omega_0\tau} \, d\tau \tag{45b}$$

We can write Eq. (44) in the c-number language by making use of the anti-normal mapping rule[6]:

$$\begin{aligned}\dot{P}(\alpha, \alpha^*, t) = \Big\{ & i\omega_0\left(\frac{\partial}{\partial\alpha}\alpha - \frac{\partial}{\partial\alpha^*}\alpha^*\right) + \frac{1}{2}\dot{C}(t)\left(\frac{\partial}{\partial\alpha}\alpha + \frac{\partial}{\partial\alpha^*}\alpha^*\right) \\ & - \frac{1}{2}\dot{C}(t)\left(\frac{\partial^2}{\partial\alpha^2}\alpha^2 + \frac{\partial^2}{\partial\alpha^{*2}}\alpha^{*2}\right) \\ & + \dot{C}(t)\frac{\partial^2}{\partial\alpha\partial\alpha^*}\alpha^*\alpha + [\phi(t) + \phi^*(t)]\frac{\partial^2}{\partial\alpha\partial\alpha^*}\Big\} P(\alpha, \alpha^*, t)\end{aligned} \tag{46}$$

Furthermore, if we introduce the polar coordinates $\alpha = re^{i\varphi}$, we can write this in a more familiar form:

$$\dot{P} = \left\{ \omega_0 \frac{\partial}{\partial \varphi} + \frac{1}{2} \left[\dot{C}(t) + \frac{\phi(t) + \phi^*(t)}{2r^2} \right] \frac{\partial^2}{\partial \varphi^2} + \frac{\phi(t) + \phi^*(t)}{4r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) \right\} P \tag{47}$$

We see from Eq. (47) that the so-called nonadiabatic effect occurs due to the amplitude modulation, in addition to the adiabatic effect represented by the term including $\dot{C}(t)$. In the narrowing limit, i.e., the long-time approximation, $t \to +\infty$, Eq. (47) reduces to the one obtained by Kubo for a "classical model of resonating *spins*."[5] Moreover, if we drop the nonadiabatic term by putting $g = 0$, Eq. (47) coincides with Kubo's equation for a classical oscillator with random frequency modulation,[5] as was discussed in the previous paper.[4]

Example (*ii*). *A Spin System Under Random Perturbations*. A spin with a randomly modulated, resonating Larmor frequency and under the influence of perpendicular random fields can be described by the stochastic Hamiltonian (13), in which

$$\mathscr{H}_0 = \omega_0 S_z \tag{48}$$

$$\mathscr{H}_1(t) = g\mathbf{R}(t)\cdot\mathbf{S} \tag{49}$$

Here $\mathbf{R}(t)$ is a random external field acting upon the spin $\mathbf{S}$. The longitudinal component $R_z(t)$ induces the frequency modulation, while the perpendicular components $R_x(t)$ and $R_y(t)$ give rise to the nonadiabatic effects.

We obtain from Eq. (42) the equation

$$\dot{\rho}(t) = -i\{1 + \delta(t)\}\omega_0[S_z, \rho(t)] + \frac{1}{2\tau_0(t)}\{[S_z\rho(t), S_z] + \text{H.c.}\} + \frac{1}{2\tau_1(t)}\{[S_x\rho(t), S_x] + [S_y\rho(t), S_y] + \text{H.c.}\} \tag{50}$$

where we have assumed rotational symmetry around the z axis and introduced

$$\delta(t) = (g^2/\omega_0)\int_0^t \langle R_x(\tau)R_x(0)\rangle_B \sin(\omega_0\tau)\, d\tau \tag{51a}$$

$$1/[2\tau_0(t)] = g^2 \int_0^t \langle R_z(\tau)R_z(0)\rangle_B\, d\tau \tag{51b}$$

and

$$1/[2\tau_1(t)] = g^2 \int_0^t \langle R_x(\tau)R_x(0)\rangle_B \cos(\omega_0\tau)\, d\tau \tag{51c}$$

The c-number equivalent of Eq. (50) can be found by virtue of the generalized phase-space method for spin operator[7] as

$$\dot{F} = \left\{ -i[1 + \delta(t)]\omega_0 L_z - \frac{L_z^2}{2\tau_0(t)} - \frac{L_x^2 + L_y^2}{2\tau_1(t)} \right\} F \tag{52}$$

or in the polar coordinate system as

$$\dot{F} = \left\{ -[1 + \delta(t)]\omega_0 \frac{\partial}{\partial\varphi} + \frac{1}{2}\left[\left(\frac{1}{\tau_0(t)} - \frac{1}{\tau_1(t)}\right) + \frac{1}{\tau_1(t)}\frac{1}{\sin^2\vartheta}\right]\frac{\partial^2}{\partial\varphi^2} + \frac{1}{2\tau_1(t)}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)\right\} F \tag{53}$$

Since the unit spin vector in the c-number space is given by

$$\mathbf{m} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta)$$

the quantity $\sin\vartheta$ in Eq. (53) is the projection of $\mathbf{m}$ onto the xy plane, and corresponds to r in example (i). We see that phase diffusion occurs due to the nonadiabatic effect in addition to the usual adiabatic broadening.

Equation (50) or Eq. (53) leads to the Bloch equation of the form

$$\frac{d}{dt}\langle S_\pm(t)\rangle = \pm i\{1 + \delta(t)\}\omega_0\langle S_\pm(t)\rangle - \frac{1}{T_2(t)}\langle S_\pm(t)\rangle \tag{54a}$$

$$\frac{d}{dt}\langle S_z(t)\rangle = -\frac{1}{T_1(t)}\langle S_z(t)\rangle \tag{54b}$$

where the relaxation-time functions $T_1(t)$ and $T_2(t)$ are defined as[8]

$$T_1(t) = \tau_1(t), \qquad \frac{1}{T_2(t)} = \frac{1}{2}\left\{\frac{1}{\tau_0(t)} + \frac{1}{\tau_1(t)}\right\} \tag{55}$$

We shall not discuss Eq. (54b) because it does not give the correct equilibrium value of $\langle S_z\rangle$ except in the high-temperature limit (see Section 5). We can easily solve Eq. (54a):

$$\langle S_-(t)\rangle = \exp\left[-i\omega_0\left\{t + \int_0^t \delta(\tau)\,d\tau\right\} - \int_0^t \frac{d\tau}{T_2(\tau)}\right]\langle S_-(0)\rangle \tag{56}$$

Or, more explicitly, if we assume, for example, force correlations of the form

$$\langle R_z(\tau)R_z(0)\rangle_B = \Delta_\parallel^2 \exp(-\gamma_\parallel|\tau|), \qquad (\gamma_\parallel = 1/\tau_{c\parallel}) \tag{57a}$$

$$\langle R_x(\tau)R_x(0)\rangle_B = \Delta_\perp^2 \exp(-\gamma_\perp|\tau|), \qquad (\gamma_\perp = 1/\tau_{c\perp}) \tag{57b}$$

we obtain the expression

$$\begin{aligned}\langle S_-(t)\rangle = \exp\Bigg[& -i\left(1 + \frac{g^2\Delta_\perp^2}{\omega_0^2 + \gamma_\perp^2}\right)\omega_0 t - i\left(\frac{g\Delta_\perp}{\omega_0^2 + \gamma_\perp^2}\right)^2 \\ & \times ((\gamma_\perp^2 - \omega_0^2)[\exp(-\gamma_\perp t)] \sin \omega_0 t \\ & + 2\omega_0\gamma_\perp\{[\exp(-\gamma_\perp t)] \cos \omega_0 t - 1\}) \\ & - \left(g^2\Delta_\parallel^2\tau_{c\parallel} + \frac{g^2\Delta_\perp^2\gamma_\perp}{\omega_0^2 + \gamma_\perp^2}\right)t + (g\Delta_\parallel\tau_{c\parallel})^2 \\ & \times [1 - \exp(-\gamma_\parallel t)] + \frac{2g^2\Delta_\perp^2\gamma_\perp\omega_0}{(\omega_0^2 + \gamma_\perp^2)^2}[\exp(-\gamma_\perp t)] \sin \omega_0 t \\ & + \frac{g^2\Delta_\perp^2(\omega_0^2 - \gamma_\perp^2)}{(\omega_0^2 + \gamma_\perp^2)^2}\{[\exp(-\gamma_\perp t)] \cos \omega_0 t - 1\}\Bigg]\langle S_-(0)\rangle \end{aligned} \tag{58}$$

This can be used to discuss not only the long-time, but also the short-time behavior. It will be discussed in a separate paper (see Section 5).

5. CONCLUDING REMARKS

We have succeeded in generalizing the derivation of our memoryless master equation for the case of a *time-dependent Hamiltonian*, and applied the master equation in its first Born approximation form to two examples which correspond to those discussed in the previous paper.[4]

We started from the stochastic Liouville equation (14) and the *time-independent projection operator* (15), and successfully reconstructed the basic equations for the stochastic theory of spectral line shape formulated by Kubo.[5] In order to proceed further, we have to extract from these equations various interesting aspects, such as those the stochastic theory has given. This extraction can be done by applying the method of time scaling, but that will be performed in another paper.

The stochastic theory has, by nature, a phenomenological character. The basic equations thus derived are not without a flaw, i.e., the well-known loss of some temperature effects. In order to remedy this, we must introduce frictional forces or the like, which cannot be incorporated into the Hamiltonian formalism: The introduction of dissipation functions is necessary. Reliable research in this direction would be difficult, especially if it is formulated quantum mechanically, although in the classical formulation Kubo and Hashitsume[8] have already given an example for the Brownian motion of a spin.

However, except for the difficulty just mentioned, the stochastic theory is considered to be useful in many practical applications in physics, and it is hoped that our new master equation will find various applications. In the Appendix we give a simple example for which our new formulation provides an essential improvement over the conventional one with memory effect.

APPENDIX. KUBO'S MODEL OF FREQUENCY MODULATION

As the simplest mathematically solvable example, let us consider Kubo's oscillator model of frequency modulation referred to in Section 3 of our previous paper. The complex coordinate $x(t)$ of this oscillator is assumed to obey the stochastic equation of motion

$$\frac{d}{dt}x(t) = i\{\omega_0 + g\omega_1(t)\}x(t) \tag{A.1}$$

where we have introduced a coupling constant g explicitly. ω_0 is a fixed characteristic frequency, while $\omega_1(t)$ is supposed to be a *stationary Gaussian process* with vanishing average. This equation of motion is not the Liouville equation, but obviously it has the same structure as the latter: $x(t)$ corresponds to $W(t)$ of Eq. (14), ω_0 to $-L_0$, and $g\omega_1(t)$ to $-L_1(t)$, i.e., Eq. (A.1) may be regarded as the mathematically simplest case with *commuting* L_0 and $L_1(t)$. The projection operator (15) in this case means to take the average over the process $\omega_1(t)$. Our assumption on this process is expressed by the characteristic functional[5]

$$\left\langle \exp\left\{ ig\int_0^t \omega_1(\tau)\zeta(\tau)\,d\tau\right\}\right\rangle_B = \exp\left\{-\tfrac{1}{2}g^2\int_0^t d\tau_1\int_0^t d\tau_2\,\Phi(\tau_1-\tau_2)\zeta(\tau_1)\zeta(\tau_2)\right\} \tag{A.2}$$

where

$$\Phi(\tau_1-\tau_2) = \langle\omega_1(\tau_1)\omega_1(\tau_2)\rangle_B \tag{A.3}$$

We are interested only in the averaged or projected coordinate

$$\mathscr{P}x(t) = \langle x(t)\rangle_B = [\exp(i\omega_0 t)]\left\langle \exp\left\{ig\int_0^t \omega_1(\tau)\,d\tau\right\}\right\rangle_B x(0) \tag{A.4}$$

Here we have assumed that the initial value $x(0)$ is fixed or independent of the process $\omega_1(t)$, i.e.

$$\mathscr{Q}x(0) = (1-\mathscr{P})x(0) = 0 \tag{A.5}$$

If we put $\zeta(\tau) = 1$ in Eq. (A.2), we obtain at once

$$\mathscr{P}x(t) = \exp\left\{i\omega_0 t - g^2\int_0^t (t-\tau)\Phi(\tau)\,d\tau\right\}x(0) \tag{A.6}$$

which is the exact solution of the projected equation of motion

$$\frac{d}{dt}\mathscr{P}x(t) = \left\{i\omega_0 - g^2\int_0^t \Phi(\tau)\, d\tau\right\}\mathscr{P}x(t) \tag{A.7}$$

Before applying our method we have to check the commutability of d/dt and $\mathscr{P}$. Since we know $d/dt\cdot\mathscr{P}$ by Eq. (A.7), we need only to calculate $\mathscr{P}\cdot d/dt$ or to prove the relation

$$\langle ig\omega_1(t)x(t)\rangle_B = -g^2\int_0^t \Phi(\tau)\, d\tau\, \mathscr{P}x(t) \tag{A.8}$$

According to Eq. (A.2), we have

$$\begin{aligned}
&\left\langle ig\omega_1(t)\exp\left\{ig\int_0^t \omega_1(\tau)\, d\tau\right\}\right\rangle_B \\
&\quad= \lim_{\zeta(\tau)\to 1} 2\frac{\delta}{\delta\zeta(t)}\left\langle \exp\left\{ig\int_0^t \omega_1(\tau)\zeta(\tau)\, d\tau\right\}\right\rangle_B \\
&\quad= \lim_{\zeta(\tau)\to 1}(-g^2)\int_0^t d\tau_1\int_0^t d\tau_2\, \Phi(\tau_1-\tau_2)\{\delta(t-\tau_1)\zeta(\tau_2)+\zeta(\tau_1)\delta(t-\tau_2)\} \\
&\qquad\times\left\langle \exp\left\{ig\int_0^t \omega_1(\tau)\zeta(\tau)\, d\tau\right\}\right\rangle_B
\end{aligned}$$

and hence the relation (A.8)

Equation (38) gives

$$\frac{d}{dt}\mathscr{P}x(t) = i\omega_0\mathscr{P}x(t) - \Psi(t)\mathscr{P}x(t) \tag{A.9}$$

with the operator

$$\Psi(t) = g\left\langle i\omega_1(t)\frac{\Sigma(t)}{1+\Sigma(t)}\right\rangle_B \tag{A.10}$$

where

$$\Sigma(t) = -g\int_0^t d\tau\, \mathscr{G}(t,\tau)i\mathscr{Q}\omega_1(\tau)\mathscr{P}G(t,\tau) \tag{A.11a}$$

$$\mathscr{G}(t,\tau) = e^{i\omega_0(t-\tau)}S(t,\tau)\mathscr{Q} \tag{A.11b}$$

$$G(t,\tau) = e^{-i\omega_0(t-\tau)}R(t,\tau) \tag{A.11c}$$

If we expand $\Sigma(t)$, $S(t,\tau)$, and $R(t,\tau)$ in powers of the coupling constant g, we have

$$\Sigma(t) = g\Sigma_1(t) + g^2\Sigma_2(t) + g^3\Sigma_3(t) + \cdots \tag{A.12}$$

where

$$\Sigma_1(t) = -\int_0^t d\tau\, i\mathscr{Q}\omega_1(\tau)\mathscr{P}$$

$$\Sigma_2(t) = -\int_0^t d\tau\, S_1(t, \tau)i\mathscr{Q}\omega_1(\tau)\mathscr{P} - \int_0^t d\tau\, i\mathscr{Q}\omega_1(\tau)\mathscr{P}R_1(t, \tau)$$

$$\Sigma_3(t) = -\int_0^t d\tau\, S_1(t, \tau)i\mathscr{Q}\omega_1(\tau)\mathscr{P}R_1(t, \tau) - \int_0^t d\tau\, S_2(t, \tau)i\mathscr{Q}\omega_1(\tau)\mathscr{P}$$
$$- \int_0^t d\tau\, i\mathscr{Q}\omega_1(\tau)\mathscr{P}R_2(t, \tau)$$

and so on. Substituting Eq. (A.12) into expression (A.10), we obtain the expansion of $\Psi(t)$:

$$\Psi(t) = g^2\Psi_2(t) + g^4\Psi_4(t) + \cdots \tag{A.13}$$

The odd-power terms vanish because of the assumption $\langle\omega_1(t)\rangle_B = 0$. In this expression we find that *the second-order term*

$$\Psi_2(t) = \langle i\omega_1(t)\Sigma_1(t)\rangle_B = \int_0^t d\tau\, \Phi(\tau) \tag{A.14a}$$

already gives the exact result (A.7). Thus the higher order terms should all vanish. This is due to our assumption of a Gaussian process. Presumably we need *not* prove this, but we will check it term by term. We do it here only for the fourth-order term,

$$\Psi_4(t) = \langle i\omega_1(t)\{\Sigma_3(t) - \Sigma_2(t)\Sigma_1(t)\}\rangle_B \tag{A.14b}$$

The first part on the right-hand side is explicitly written as

$$\begin{aligned}
&\langle i\omega_1(t)\Sigma_3(t)\rangle_B \\
&= -\int_0^t d\tau \int_\tau^t dt_1 \int_\tau^{t_1} dt_2\, \langle i\omega_1(t)i\mathscr{Q}\omega_1(t_1)i\mathscr{Q}\omega_1(t_2)i\mathscr{Q}\omega_1(\tau)\rangle_B \\
&\quad - \tfrac{1}{2}\int_0^t d\tau\, \langle i\omega_1(t)i\omega_1(t)\rangle_B \int_\tau^t dt_1 \int_\tau^t dt_2\, \langle i\omega_1(t_1)i\omega_1(t_2)\rangle_B \\
&= -\int_0^t d\tau \int_\tau^t dt_1 \int_\tau^{t_1} dt_2\, \{\Phi(t - t_2)\Phi(t_1 - \tau_3) + \Phi(t - \tau_3)\Phi(t_1 - t_2)\} \\
&\quad -\tfrac{1}{2}\int_0^t d\tau \int_\tau^t dt_1 \int_\tau^t dt_2\, \Phi(t - \tau)\Phi(t_1 - t_2)
\end{aligned}$$

and the second part as

$$\langle i\omega_1(t)\Sigma_2(t)\Sigma_1(t)\rangle_B = -\int_0^t dt_1 \int_0^t dt_2 \int_{t_1}^t dt_3\, \Phi(t - t_1)\Phi(t_3 - t_2)$$

We can easily transform the integrals to get the same form

$$\langle i\omega_1(t)\Sigma_3(t)\rangle_B = \langle i\omega_1(t)\Sigma_2(t)\Sigma_1(t)\rangle_B$$
$$= -\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{\Phi(t - t_2)\Phi(t_1 - t_3)$$
$$+ 2\Phi(t - t_3)\Phi(t_1 - t_2)\} \tag{A.15}$$

and hence we have proved that

$$\Psi_4(t) = 0 \tag{A.16}$$

By the traditional damping theory, or from Eqs. (16a) and (18), we obtain the projected equation of motion with the memory effect

$$\frac{d}{dt}\mathscr{P}x(t) = i\omega_0\mathscr{P}x(t) - \int_0^t d\tau\, X(t - \tau)\mathscr{P}x(\tau) \tag{A.17}$$

where the kernel is given by

$$X(t - \tau) = g^2\langle\omega_1(t)\mathscr{G}(t, \tau)\mathscr{Q}\omega_1(\tau)\rangle_B$$
$$= g^2X_2(t - \tau) + g^4X_4(t - \tau) + \cdots \tag{A.18}$$

Now the lowest order kernel is

$$X_2(t - \tau) = \Phi(t - \tau)e^{i\omega_0(t-\tau)} \tag{A.19}$$

and thus *our exact equation* (A.7) *is not reached within this approximation.* We must proceed to higher order terms to obtain a good approximation, except in the narrowing limit $\alpha \to 0$ with t/t_r fixed, where we have introduced parameters

$$\Delta = \langle\omega_1{}^2\rangle_B^{1/2}, \qquad \tau_c = (1/\Delta^2)\int_0^\infty d\tau\, \Phi(\tau), \qquad 1/\tau_r = g^2\Delta^2\tau_c \tag{A.20a}$$

and

$$\alpha = g\,\Delta\tau_c \tag{A.20b}$$

$g\Delta$ gives the mean amplitude of frequency modulation, τ_c is the coherence time of modulation, τ_r is the relaxation time of the coordinate $x(t)$ in the narrowing limit, and α is the parameter characterizing the intensity and speed of modulation, as was discussed by Kubo in detail.[5]

To see the situation more explicitly, let us further assume that the process $\omega_1(t)$ is Markovian, i.e.,

$$\Phi(\tau) = \Delta^2 e^{-|\tau|/\tau_c} \tag{A.21}$$

Then the exact equation (A.7) or the second-order equation with $\Psi_2(t)$, (A.14a), and its exact solution (A.6) become, respectively,

$$\frac{d}{dt}\mathscr{P}x(t) = \left\{i\omega_0 - \frac{1}{\tau_r}(1 - e^{-t/\tau_c})\right\}\mathscr{P}x(t) \tag{A.22}$$

and

$$\mathscr{P}x(t) = \exp\left\{i\omega_0 t - \alpha^2\left(\frac{t}{\tau_c} + e^{-t/\tau_c} - 1\right)\right\}x(0) \tag{A.23}$$

On the other hand, the second-order equation obtained from the non-Markovian equation (A.17) with the Born approximation kernel (A.19) is

$$\frac{d}{dt}\mathscr{P}x(t) = i\omega_0\mathscr{P}x(t) - (g\Delta)^2\int_0^t d\tau \exp\left\{\left(i\omega_0 - \frac{1}{\tau_c}\right)(t-\tau)\right\}\mathscr{P}x(\tau) \tag{A.24}$$

and has the solution

$$\mathscr{P}x(t) = \frac{\exp(i\omega_0 t)}{2(1-4\alpha^2)^{1/2}}\left\{[1 + (1-4\alpha^2)^{1/2}]\exp\left(-\frac{[1-(1-4\alpha^2)^{1/2}]t}{2\tau_c}\right)\right.$$
$$\left. - [1 - (1-4\alpha^2)^{1/2}]\exp\left(-\frac{[1+(1-4\alpha^2)^{1/2}]t}{2\tau_c}\right)\right\}x(0) \tag{A.25}$$

For $\alpha \to 0$ with t/τ_r fixed, we have

$$\mathscr{P}x(t) \sim [\exp(i\omega_0 t)]\{(1+\alpha^2)\exp(-t/\tau_r) - \alpha^2\exp[-(\alpha^{-2} - 1)t/\tau_r]\}x(0) \tag{A.26}$$

The solution (A.25) is quite different for small $t \leqslant \tau_c$ from the exact solution (A.23), which under that condition has the form[5]

$$\mathscr{P}x(t) \sim \exp\left\{i\omega_0 t - \frac{(g\Delta)^2}{2}t^2 + \cdots\right\}x(0) \tag{A.27}$$

This suggests the danger, in this model at least, of investigating the memory effect by using the truncated non-Markovian equation of motion. Only in the narrowing limit $\tau_c \ll t \sim \tau_r$ may we expect the solution (A.25) or (A.26) to be in accord with the exact one, both giving[5]

$$\mathscr{P}x(t) \sim e^{i\omega_0 t - t/\tau_r}x(0) \tag{A.28}$$

ACKNOWLEDGMENTS

The authors are indebted to Prof. R. Kubo for valuable discussions and a careful reading of the manuscript. We are also grateful to Dr. P. Hänggi for informing us of some of the earlier references on the memoryless master equation.

REFERENCES

1. R. Zwanzig, *Physica* **30**:1109 (1964); F. Haake, in *Springer Tracts in Modern Physics*, No. 66 (1973), p. 98; R. Kubo, in *Lectures at Sitges International School of Statistical Mechanics, 1974*, L. Garrid, ed. (Springer Verlag, Berlin, 1975), and references cited therein.
2. M. Tokuyama and H. Mori, *Prog. Theor. Phys.* **55**:411 (1976).
3. A. Fulinski and W. J. Kramarczyk, *Physica* **39**:575 (1968); T. Shimizu, *J. Phys. Soc. Japan* **28**:1088 (1970); V. P. Vstovsky, *Phys. Lett.* **44**:283 (1973).
4. N. Hashitsume, F. Shibata, and M. Shingū, *J. Stat. Phys.* **17**:155 (1977).
5. R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, D. ter Haar, ed. (Oliver and Boyd, Edinburgh, 1962), p. 23; *J. Math. Phys.* **4**:174 (1963); *Adv. Chem. Phys.* **16**:101 (1969).
6. R. J. Glauber, *Phys. Rev.* **131**:2766 (1963); G. S. Agarwal and E. Wolf, *Phys. Rev. D* **2**:2161, 2187, 2206 (1970).
7. Y. Takahashi and F. Shibata, *J. Phys. Soc. Japan* **38**:656 (1975); *J. Stat. Phys.* **14**:49 (1976).
8. R. Kubo and N. Hashitsume, *Prog. Theor. Phys. Suppl.* **46**:210 (1970).

NOTE ADDED IN PROOF

Additional references: For another approach to non-Markovian effects.

9. P. Hänggi and H. Thomas, *Z. Phys. B.* **26**:85 (1977).
10. H. Grabert, P. Talkner, and P. Hänggi, *Z. Phys. B.* **26**:389 (1977).

Our term "memoryless" should be replaced by "convolutionless".