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Quantal Master Equation Valid for Any Time Scale

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A new memoryless expression for the equation of motion for the reduced density matrix is derived. It is equivalent to that proposed by Tokuyama and Mori, but has a more convenient form for the application of the perturbational expansion method. The master equation derived from this form of equation in the first Born approximation is applied to two examples, the Brownian motion of a quantal oscillator and that of a spin. In both examples the master equation is rewritten into the coherent-state representation. A comparison is made with the stochastic theory of the spectral line shape given by Kubo, and it is shown that this theory of the line shape can be incorporated into the framework of the present theory.

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

1. INTRODUCTION

In nonequilibrium statistical mechanics various kinds of treatments have been devised to obtain the master equation for a probability distribution function or the Langevin equations for relevant physical quantities.[1,2] As a result of recent developments in laser physics, quantum optics, and other fields of nonequilibrium research, these equations have become rather familiar and have been found to provide useful tools.[3-5] However, most of these treatments are formulated on the basis of the so-called damping theory, and whether we use the Schrödinger picture or proceed with the Heisenberg picture, we obtain *equations with memory*. In general, it is a formidable task to take the non-Markovian effects into account[6] and in practical applications we must almost always be content with the narrowing limit where the memory effects are completely neglected.

However, in the stochastic theory of the spectral line shape formulated by Kubo,[7] restrictions such as the narrowing condition are removed, and

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we can discuss overall features of the resonance absorption, although the theory itself is of a phenomenological nature. It is highly desirable to construct a microscopic theory that is free from the restrictions mentioned above and is useful for any time scale, as the stochastic theory is. Fortunately, a new type of expression was recently proposed by Tokuyama and Mori for the equation of motion.[8] A very important characteristic of this expression is its *memoryless* structure, and the theory based on it shares some aspects with the stochastic theory of Kubo. Tokuyama and Mori used the Langevin equation approach in the Heisenberg picture, introducing the microscopic phase density represented by a delta function as the relevant dynamical variable. However, unfortunately, their theory is mostly confined to the classical cases, and furthermore, time-dependent Hamiltonians are introduced without any modification, which is necessary for the above-mentioned new expression. Moreover, it has been recognized that the use of the operator delta function involves much mathematical complexity, especially in the Heisenberg picture.

Thus, in the present paper we formulate the problem in the Schrödinger picture, and derive a new expression of the quantal Liouville equation, which is equivalent to that of Tokuyama and Mori but is more convenient for the perturbational analysis to obtain the master equation. An operator form of equation for the reduced density matrix can be transcribed into the c-number one by making use of the generalized phase-space method.[9–11] The resulting equation for the quasiprobability distribution function has a structure quite analogous to that of the classical one, and, as is well known, is suitable for obtaining the corresponding classical expression. We do this transcription for two model cases and reduce the dynamical aspect of the nonlinear problems to a feasible form in the c-number formalism.

In Section 2 we derive a generalized master equation for the density matrix of a system in contact with a heat reservoir in a form convenient for the perturbational analysis. Next in Section 3 as a simple application we discuss the Brownian motion of a quantal oscillator and its phase diffusion,[12] and in Section 4 we investigate a somewhat complicated problem of the Brownian motion of a spin.[10,13] Finally in Section 5 we give a few remarks. We use units where $\hbar = 1$.

2. GENERALIZED MASTER EQUATION IN OPERATOR SPACE

We consider a total system composed of the system under consideration and a heat reservoir. The system is assumed to have a Hamiltonian $\mathscr{H}_S$, and the reservoir a Hamiltonian $\mathscr{H}_B$. An interaction between them is represented by $\mathscr{H}_{SB}$. All these operators are assumed to be *time independent*.

The time evolution of the total system is governed by the quantal Liouville equation for the total density matrix $W(t)$:

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

where L denotes the Liouville operator

$$L = L_S + L_B + L_{SB} \tag{2}$$

corresponding to the total Hamiltonian

$$\mathscr{H} = \mathscr{H}_S + \mathscr{H}_B + \mathscr{H}_{SB} \tag{3}$$

In order to eliminate irrelevant variables associated with the reservoir, we introduce a *time-independent* projection operator $\mathscr{P}$. We can easily derive from Eq. (1) our memoryless form of the evolution equation for the projected density matrix $\mathscr{P}W(t)$:

$$\begin{aligned}\mathscr{P}\dot{W}(t) = & -i\mathscr{P}L\mathscr{P}W(t) - i\mathscr{P}L\{\theta(t) - 1\}\mathscr{P}W(t) \\ & - i\mathscr{P}L\theta(t)e^{-i\mathscr{Q}Lt}\mathscr{Q}W(0)\end{aligned} \tag{4}$$

where we have put $\mathscr{Q} = 1 - \mathscr{P}$ and defined an operator

$$\theta(t) = [1 - \mathscr{Q}(1 - e^{-i\mathscr{Q}Lt}\mathscr{Q}e^{iLt})]^{-1} \tag{5}$$

We give a short derivation of Eq. (4) in Appendix A. Expression (4) can be rewritten into the form proposed by Tokuyama and Mori,[8] as is shown also in Appendix A.

As the explicit form of the projection operator $\mathscr{P}$, which is not necessary for the derivation of (4), we take, as usual,[2,4]

$$\mathscr{P}X = \rho_B \operatorname{tr}_B X \tag{6}$$

where the operator ρ_B in the reservoir space is introduced to ensure the idempotent property $\mathscr{P}^2 = \mathscr{P}$ and in consequence has to satisfy the normalization condition

$$\operatorname{tr}_B \rho_B = 1 \tag{7}$$

Here tr_B denotes the trace in the reservoir space. The reduced density matrix for the system is of course defined as

$$\rho(t) = \operatorname{tr}_B W(t) \tag{8}$$

We see that L_S and L_B commute with $\mathscr{P}$ and hence with $\mathscr{Q}$:

$$\begin{aligned}\mathscr{P}L_S &= L_S\mathscr{P}, \qquad \mathscr{P}L_B = L_B\mathscr{P} = 0 \\ \mathscr{Q}L_S &= L_S\mathscr{Q} \qquad \mathscr{Q}L_B = L_B\mathscr{Q} = L_B\end{aligned} \tag{9}$$

and that

$$\mathscr{P}W(t) = \rho_B \cdot \rho(t) \tag{10}$$

If we introduce the notation

$$\langle \cdots \rangle_B = \mathrm{tr}_B(\cdots \rho_B) \tag{11}$$

we obtain our final expression for the equation of motion for the reduced density matrix of the system:

$$\dot{\rho}(t) = -i(L_S + \langle L_{SB} \rangle_B)\rho(t) - \Psi(t)\rho(t) \tag{12}$$

where we have introduced an operator

$$\Psi(t) = \langle iL\{\theta(t) - 1\}\rangle_B \tag{13}$$

and assumed for simplicity the usual initial condition

$$\mathscr{Q}W(0) = 0, \qquad \text{or} \qquad W(0) = \rho_B \cdot \rho(0) \tag{14}$$

Our next task is to rewrite the expression for the operator $\Psi(t)$ into a more tractable form for the perturbational analysis. We transform the operators e^{iLt} and $e^{-i\mathscr{Q}Lt}$ in the operator $\theta(t)$ in the spirit of perturbation theory.[14] If we introduce the unperturbed evolution operator

$$U_0(t) = e^{-i(L_s + L_B)t} \tag{15}$$

we can determine the evolution operator in the interaction picture through the definition

$$e^{-iLt} = U_0(t)R(t) \tag{16}$$

as

$$R(t) = \mathrm{T}_{\leftarrow} \exp\left[-i\int_0^t d\tau U_0(-\tau)L_{SB}U_0(\tau)\right] \tag{17}$$

Here $\mathrm{T}_{\leftarrow}$ is the chronological ordering operator. We note that $U_0(t)$ commutes with $\mathscr{P}$ and $\mathscr{Q}$ by virtue of Eqs. (9). In a similar way we can determine a new evolution operator $S(t)$ through the definition

$$e^{-i\mathscr{Q}L\mathscr{Q}t} = S(t)V_0(t) \tag{18}$$

with an unperturbed operator

$$V_0(t) = e^{-i\mathscr{Q}(L_s + L_B)\mathscr{Q}t} = \mathscr{P} + \mathscr{Q}U_0(t)\mathscr{Q} \tag{19}$$

It is easy to show that

$$S(t) = \mathrm{T}_{\rightarrow} \exp\left[-i\int_0^t d\tau \mathscr{Q}U_0(\tau)L_{SB}U_0(-\tau)\mathscr{Q}\right] \tag{20}$$

where $\mathrm{T}_{\rightarrow}$ denotes the antichronological operator. In contrast to Eq. (16), we have put $S(t)$ on the left of $V_0(t)$ in Eq. (18). This is only for the purpose of writing the expression of $\theta(t)$ in a simpler way. The structure of $S(t)$ shows that $S(t)$ commutes with $\mathscr{Q}$, whence we have the relation

$$e^{-i\mathscr{Q}Lt}\mathscr{Q} = \mathscr{Q}e^{-i\mathscr{Q}L\mathscr{Q}t} = \mathscr{Q}S(t)U_0(t) \tag{21}$$

Then the operator $\theta(t)$ can be written in the form

$$\theta(t) = [1 + \mathscr{Q}\{S(t)R(-t) - 1\}]^{-1} \tag{22}$$

Substituting this expression for $\theta(t)$ into Eq. (13), we obtain the desired expression for $\Psi(t)$:

$$\Psi(t) = -i\left\langle L_{SB}\frac{\mathscr{Q}\{S(t)R(-t) - 1\}}{1 + \mathscr{Q}\{S(t)R(-t) - 1\}}\right\rangle_B \tag{23}$$

Equation (12) with this expression for $\Psi(t)$ is exact, within the range of the initial condition (14), and has a form convenient for the perturbational expansion in powers of L_{SB}. In subsequent sections, we shall confine ourselves to the usual perturbational expression, which is valid up to $O(L_{SB}{}^2)$. In this Born approximation, since we have already one factor L_{SB} explicitly in expression (23), we may put $S(t) = R(-t) = 1$ in the denominator and are required to determine the product $S(t)R(-t)$ in the numerator up to $O(L_{SB})$:

$$\mathscr{Q}\{S(t)R(-t) - 1\} = i\int_0^t d\tau \mathscr{Q}U_0(\tau)L_{SB}U_0(-\tau)\mathscr{P} \tag{24}$$

Thus we have the approximate expression

$$\Psi(t) = \int_0^t d\tau \langle L_{SB}\mathscr{Q}U_0(\tau)L_{SB}\rangle_B e^{iL_s\tau} \tag{25}$$

In the conventional treatment of the damping theory one has the equation with memory [obtained from Eq. (60)]

$$\dot{\rho}(t) = -i(L_S + \langle L_{SB}\rangle_B)\rho(t) - \int_0^t d\tau \langle L_{SB}e^{-i\mathscr{Q}L\tau}\mathscr{Q}L_{SB}\rangle_B \rho(t - \tau) \tag{26}$$

or, within the Born approximation,

$$\dot{\rho}(t) = -i(L_S + \langle L_{SB}\rangle_B)\rho(t) - \int_0^t d\tau \langle L_{SB}\mathscr{Q}U_0(\tau)L_{SB}\rangle_B \rho(t - \tau) \tag{27}$$

One usually either neglects the time displacement τ in $\rho(t - \tau)$ by assuming the narrowing limit or puts approximately $\rho(t - \tau) = e^{iL_s\tau}\rho(t)$. These ambiguous assumptions are not necessary in our treatment. Equation (25) is exact within the Born approximation. We find that the conventional approximation $\rho(t - \tau) = e^{iL_s\tau}\rho(t)$ leads rather to the exact result.

3. BROWNIAN MOTION OF A QUANTAL OSCILLATOR. RANDOM FREQUENCY MODULATION

As a first application, let us consider a quantal oscillator weakly interacting with a heat reservoir, which is assumed to be large enough and to stay always in its thermal equilibrium. We *do not* impose any such requirement as, for instance, making the correlation time of the reservoir much shorter than the relaxation time of the system.

In the Hamiltonian (3) we take

$$\mathscr{H}_S = \omega_0 b^\dagger b \tag{28a}$$

and

$$\mathscr{H}_{SB} = g(bB^\dagger + b^\dagger B) + g' b^\dagger b \Gamma \tag{28b}$$

where the Bose operators b and $b^\dagger$ represent the quantal oscillator, and B and $B^\dagger$ are the reservoir operators: Usually one takes Γ as $B^\dagger B$. The reservoir Hamiltonian $\mathscr{H}_B$ need not be explicitly specified. Because of the condition imposed on the reservoir we may use for ρ_B the unperturbed canonical form

$$\rho_B = e^{-\beta \mathscr{H}_B}/\mathrm{tr}_B(e^{-\beta \mathscr{H}_B}) \tag{29}$$

We neglect a time-independent shift from ω_0 and assume

$$\mathscr{P} L_{SB} \mathscr{P} = 0 \tag{30}$$

Then Eq. (12) with expression (25) reduces to

$$\dot{\rho}(t) = -i[\mathscr{H}_S, \rho(t)] + \int_0^t d\tau \, \mathrm{tr}_B\{[\mathscr{H}_{SB}, \rho(t)\rho_B \mathscr{H}_{SB}(-\tau)] + \mathrm{H.c.}\} \tag{31}$$

where

$$\mathscr{H}_{SB}(\tau) = e^{i(\mathscr{H}_s + \mathscr{H}_B)\tau} \mathscr{H}_{SB} e^{-i(\mathscr{H}_s + \mathscr{H}_B)\tau} \tag{32}$$

More explicitly we find

$$\begin{aligned} \dot{\rho}(t) = & -i\omega_0[b^\dagger b, \rho(t)] \\ & + \phi^*_{+-}(t)[b^\dagger, \rho(t)b] + \phi^*_{-+}(t)[b, \rho(t)b^\dagger] \\ & + \phi_{+-}(t)[b^\dagger \rho(t), b] + \phi_{-+}(t)[b\rho(t), b^\dagger] \\ & + \phi_0^*(t)[b^\dagger b, \rho(t)b^\dagger b] + \phi_0(t)[b^\dagger b\rho(t), b^\dagger b] \end{aligned} \tag{33}$$

where the $\phi(t)$ are given by

$$\phi_{+-}(t) = g^2 \int_0^t d\tau e^{-i\omega_0\tau} \langle B^\dagger(\tau)B(0)\rangle_B \tag{34a}$$

$$\phi_{-+}(t) = g^2 \int_0^t d\tau e^{+i\omega_0\tau} \langle B(\tau)B^\dagger(0)\rangle_B \tag{34b}$$

$$\phi_0(t) = g'^2 \int_0^t d\tau \langle \Gamma(\tau)\Gamma(0)\rangle_B \tag{34c}$$

The operator equation (6) can now be transformed into a c-number one with the aid of the coherent-state representation.[9] If we use the antinormal ordering of operators, the necessary transcription rules are

$$\rho b \to (\alpha - \partial/\partial\alpha^*)P(\alpha, \alpha^*) \tag{35a}$$

$$b\rho \to \alpha P(\alpha, \alpha^*) \tag{35b}$$

$$\rho b^\dagger \to \alpha^* P(\alpha, \alpha^*) \tag{35c}$$

and

$$b^\dagger \rho \to (\alpha^* - \partial/\partial\alpha)P(\alpha, \alpha^*) \tag{35d}$$

Thus we obtain the following master equation for the quasiprobability function $P(\alpha, \alpha^*, t)$:

$$\begin{aligned}\dot{P}(\alpha, \alpha^*, t) = \Big\{ & i\Big[\omega_0 + \Psi'(t) + \frac{1}{2}\Psi_0(t)\Big]\Big(\frac{\partial}{\partial\alpha}\alpha - \frac{\partial}{\partial\alpha^*}\alpha^*\Big) \\ & + \Big[\Psi''(t) + \frac{1}{2}\Phi_0(t)\Big]\Big(\frac{\partial}{\partial\alpha}\alpha + \frac{\partial}{\partial\alpha^*}\alpha^*\Big) \\ & + i\Psi_0(t)\Big(\frac{\partial}{\partial\alpha}\alpha - \frac{\partial}{\partial\alpha^*}\alpha^*\Big)\alpha^*\alpha - \frac{1}{2}\Phi_0(t)\Big(\frac{\partial^2}{\partial\alpha^2}\alpha^2 + \frac{\partial^2}{\partial\alpha^{*2}}\alpha^{*2}\Big) \\ & - \frac{1}{2}i\Psi_0(t)\Big(\frac{\partial^2}{\partial\alpha^2}\alpha^2 - \frac{\partial^2}{\partial\alpha^{*2}}\alpha^{*2}\Big) + \Phi_0(t)\frac{\partial^2}{\partial\alpha^*\partial\alpha}\alpha^*\alpha \\ & + [\Phi'(t) - \Psi''(t)]\frac{\partial^2}{\partial\alpha^*\partial\alpha}\Big\}P(\alpha, \alpha^*, t)\end{aligned} \tag{36}$$

where

$$\begin{aligned}\Psi(t) &= (g^2/i)\int_0^t d\tau e^{-i\omega_0\tau}\langle[B^\dagger(\tau), B]\rangle_B \\ &= (1/i)\{\phi_{+-}(t) - \phi^*_{-+}(t)\} \equiv \Psi'(t) + i\Psi''(t)\end{aligned} \tag{37a}$$

$$\begin{aligned}\Phi(t) &= g^2\int_0^t d\tau e^{-i\omega_0\tau}\langle\{B^\dagger(\tau), B\rangle_B \\ &= \phi_{+-}(t) + \phi^*_{-+}(t) \equiv \Phi'(t) + i\Phi''(t)\end{aligned} \tag{37b}$$

$$\Psi_0(t) = (g'^2/i)\int_0^t d\tau\langle[\Gamma(\tau), \Gamma(0)]\rangle_B \tag{37c}$$

and

$$\Phi_0(t) = g'^2\int_0^t d\tau\langle\{\Gamma(\tau), \Gamma(0)\}\rangle_B \tag{37d}$$

Equation (36) gives a generalization of the conventional result for the damped harmonic oscillator, and reduces for a large enough t to the usual expression in the narrowing limit.[12]

It may be interesting to compare our results with those derived from Kubo's stochastic Liouville equation. Kubo considered an oscillator whose frequency is subject to random modulation[7]:

$$\dot{x}(t) = i\{\omega_0 + \omega_1(t)\}x(t)$$

or

$$\dot{\varphi}(t) = \omega_1(t)$$

when we use the phase angle $\varphi(t)$ defined by

$$x(t) = e^{i\omega_0 t + i\varphi(t)}x(0)$$

If the stochastic process $\omega_1(t)$ is assumed to be Gaussian, the transition probability of finding $\varphi(t) = \varphi$ at a time t after it has been φ' at $t = 0$ is given by

$$f(\varphi, t\,|\,\varphi', 0) = \exp\{\tfrac{1}{2}C(t)\,\partial^2/\partial\varphi^2\}\,\delta(\varphi - \varphi') \tag{38}$$

with

$$C(t) = 2\int_0^t d\tau(t - \tau)\langle\omega_1(\tau)\omega_1(0)\rangle \tag{39}$$

Clearly, the transition probability (38) satisfies the diffusion equation

$$\dot{f}(\varphi, t) = \frac{1}{2}\,\dot{C}(t)\,\frac{\partial^2}{\partial\varphi^2}f(\varphi, t) \tag{40}$$

with the *time-dependent diffusion coefficient*

$$\dot{C}(t) = 2\int_0^t d\tau\langle\omega_1(\tau)\omega_1(0)\rangle \tag{41}$$

In our quantal oscillator, the corresponding random frequency modulation arises from the g' term in the interaction $\mathscr{H}_{SB}$; therefore we will drop the g term. The Gaussian process assumption corresponds exactly to our Born approximation. By the change of variables

$$\alpha = re^{i\varphi}$$

we can rewrite Eq. (36) as

$$\begin{aligned}\dot{P}(\alpha, \alpha^*, t) = \Bigg\{&[\omega_0 + \Psi'(t)]\frac{\partial}{\partial\varphi} + \Psi''(t)\,\frac{1}{r}\frac{\partial}{\partial r}\,r^2 \\ &+ \Psi_0(t)\left(1 - \frac{1}{2r}\frac{\partial}{\partial r}\right)r^2\,\frac{\partial}{\partial\varphi} \\ &+ [\Phi'(t) - \Psi''(t)]\,\frac{1}{4r^2}\left(r\frac{\partial}{\partial r}\,r\frac{\partial}{\partial r} + \frac{\partial^2}{\partial\varphi^2}\right) \\ &+ \frac{1}{2}\,\Phi_0(t)\,\frac{\partial^2}{\partial\varphi^2}\Bigg\}P(\alpha, \alpha^*, t)\end{aligned} \tag{42}$$

Defining the quasiprobability distribution on a rotating coordinate system

$$F(\varphi, t) = [\exp(-\omega_0 t\, \partial/\partial\varphi)]P(\alpha, \alpha^*, t)$$

and setting $g = 0$, we obtain our diffusion equation

$$\dot{F}(\varphi, t) = \frac{1}{2}\, \Phi_0(t) \frac{\partial^2}{\partial\varphi^2} F(\varphi, t) \tag{43}$$

in the classical limit, $\beta \to 0$, in which the leading terms of the Ψ's are $O(\beta)$ while those of the Φs are $O(1)$. We see the complete correspondence between Eq. (40) with the coefficient (41) and Eq. (43) with the coefficient (37). Thus we have established an important relationship between the stochastic theory of Kubo and our microscopic theory. This means that our master equation can surely be used not only for the narrowing limit, but also for short-time phenomena.

4. NONLINEAR SPIN RELAXATION

As a second application, let us consider the Brownian motion of a quantal spin interacting with a heat reservoir and under an applied static magnetic field $\mathbf{H}_0$ in the z direction. In the Hamiltonian (3) we take

$$\mathscr{H}_S = \omega_0 S_z \qquad (\omega_0 = \gamma H_0) \tag{44a}$$

and

$$\mathscr{H}_{SB} = g\mathbf{S}\cdot\mathbf{R} \tag{44b}$$

where $\mathbf{R}$ represents an effective field acting upon the spin $\mathbf{S}$ due to the motion of the reservoir. We assume again Eqs. (29) and (30) and, using the relation

$$e^{iL_s t} S_\pm = S_\pm e^{\pm i\omega_0 t} \tag{45}$$

we obtain from Eq. (31) the master equation

$$\begin{aligned} \dot{\rho}(t) = {} & -i\omega_0[S_z, \rho(t)] + \phi^*_{+-}(t)[S_+, \rho(t)S_-] + \phi^*_{-+}(t)[S_-, \rho(t)S_+] \\ & + \phi_{+-}(t)[S_+\rho(t), S_-] + \phi_{-+}(t)[S_-\rho(t), S_+] \\ & + \phi^*_{zz}(t)[S_z, \rho(t)S_z] + \phi_{zz}(t)[S_z\rho(t), S_z] \end{aligned} \tag{46}$$

where we have introduced

$$\phi_{+-}(t) = \tfrac{1}{4}g^2 \int_0^t d\tau e^{-i\omega_0\tau}\langle R_+(\tau)R_-(0)\rangle_B \tag{47a}$$

$$\phi_{-+}(t) = \tfrac{1}{4}g^2 \int_0^t d\tau e^{i\omega_0\tau}\langle R_-(\tau)R_+(0)\rangle_B \tag{47b}$$

and

$$\phi_{zz}(t) = g^2 \int_0^t d\tau\langle R_z(\tau)R_z(0)\rangle_B \tag{47c}$$

The transcription of the operator equation (46) into the one in the phase-space description can be performed by the generalized phase-space method for the spin operators.[10,11] In particular, a product of the spin operator $\mathbf{S}$ and an arbitrary operator G is mapped onto the c-number space according to the rules

$$\mathbf{S}G \to \vec{\mathscr{S}}^{(\Omega)}F^{(\Omega)} \tag{48a}$$

and

$$G\mathbf{S} \to \vec{\mathscr{S}}^{(\Omega)*}F^{(\Omega)} \tag{48b}$$

where the superscript Ω specifies the rule of association and $\mathscr{S}^{(\Omega)}$ is explicitly represented by

$$\mathscr{S}^{(\Omega)} = \tfrac{1}{2}\mathbf{L} + \mathbf{M}^{(\Omega)} \tag{49}$$

with

$$\mathbf{M}^{(N)} = S\mathbf{m} - \tfrac{1}{2}i\mathbf{m} \times \mathbf{L} \qquad (\text{for } \Omega = \text{normal ordering}) \tag{50a}$$

or with

$$\mathbf{M}^{(A)} = (S + 1)\mathbf{m} + \tfrac{1}{2}i\mathbf{m} \times \mathbf{L} \qquad (\text{for } \Omega = \text{antinormal ordering}) \tag{50b}$$

Here $\mathbf{m}$ denotes the unit vector

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

and $\mathbf{L}$ is the operator for the *orbital angular momentum.*

Let the c-number equivalent of $\rho(t)$ be $F^{(\Omega)}(\mathbf{m}, t)$. Then the association rule (49) enables us to transform Eq. (46) into the following phase-space form:

$$\begin{aligned}\{\partial/\partial t &+ i[\omega_0 - \Phi''_{+-}(t)]L_z + \Phi'_{+-}(t)(L_x{}^2 + L_y{}^2) + \tfrac{1}{2}\Phi_{zz}(t)L_z{}^2 \\ &- i[2\Psi'_{+-}(t) - \Psi_{zz}(t)]L_zM_z^{(\Omega)} - 2i\Psi''_{+-}(t) \\ &\times [L_xM_y^{(\Omega)} - L_yM_x^{(\Omega)}]\}F^{(\Omega)}(\mathbf{m}, t) = 0\end{aligned} \tag{51}$$

where we have defined the correlation functions

$$\begin{aligned}\Psi_{+-}(t) &= (g^2/4i)\int_0^t d\tau e^{-i\omega_0\tau}\langle[R_+(\tau), R_-]\rangle_B \\ &= (1/i)[\phi_{+-}(t) - \phi^*_{-+}(t)] \equiv \Psi'_{+-}(t) + i\Psi''_{+-}(t)\end{aligned} \tag{52a}$$

$$\Psi_{zz}(t) = (g^2/i)\int_0^t d\tau\langle[R_z(\tau), R_z]\rangle_B = (1/i)[\phi_{zz}(t) - \phi^*_{zz}(t)] \tag{52b}$$

$$\begin{aligned}\Phi_{+-}(t) &= \tfrac{1}{4}g^2\int_0^t d\tau e^{-i\omega_0\tau}\langle\{R_+(\tau), R_-\}\rangle_B \\ &= \phi_{+-}(t) + \phi^*_{-+}(t) \equiv \Phi'_{+-}(t) + i\Phi''_{+-}(t)\end{aligned} \tag{52c}$$

and

$$\Phi_{zz}(t) = g^2 \int_0^t d\tau \langle \{R_z(t), R_z\} \rangle_B = \phi_{zz}(t) + \phi_{zz}^*(t) \tag{52d}$$

In the derivation of Eq. (51), we have made use of the relations

$$\mathbf{L} \cdot \mathbf{m} = 0, \qquad \mathbf{L} \cdot (\mathbf{m} \times \mathbf{L}) = 0 \tag{53}$$

and

$$\mathbf{L} \cdot \mathbf{M}^{(\Omega)} = 0 \tag{54}$$

which are proved in Appendix B. The master equation (51) may be written in the following simpler form:

$$\begin{aligned} \{\partial/\partial t + i\mathbf{L}\cdot\gamma\mathbf{H}_0[1 + \delta(t) + \kappa(t)\mathbf{H}_0\cdot\mathbf{M}^{(\Omega)}] \\ - i\mathbf{L}\cdot\mathbf{D}(t)\cdot i\mathbf{L} + \eta(t) i\mathbf{L}\cdot(\mathbf{M}^{(\Omega)} \times \mathbf{H}_0)\} F^{(\Omega)}(\mathbf{m}, t) = 0 \end{aligned} \tag{55}$$

where we have put

$$\delta(t) = -\Phi''_{+-}(t)/\omega_0 \tag{56a}$$

$$\kappa(t) = \gamma[\Psi''_{zz}(t) - 2\Psi''_{+-}(t)]/\omega_0^2 \tag{56b}$$

$$\eta(t) = -2\gamma\Psi'''_{+-}(t)/\omega_0 \tag{56c}$$

and

$$\mathbf{D}(t) = \frac{1}{2}\begin{pmatrix} 1/\tau_1(t) & 0 & 0 \\ 0 & 1/\tau_1(t) & 0 \\ 0 & 0 & 1/\tau_0(t) \end{pmatrix} \tag{56d}$$

with

$$1/\tau_1(t) = 2\Phi'_{+-}(t), \qquad 1/\tau_0(t) = \Phi'_{zz}(t) \tag{57}$$

It should again be emphasized that Eq. (55) is equivalent to the original operator equation (46), although it has been transformed into the c-number language. Quantum effects appear through the definitions of the coefficients (56)–(57) and of the expression $\mathbf{M}^{(\Omega)}$.

In the narrowing limit, where we are allowed to extend t appearing in Eqs. (56a)–(56d) to infinity, Eq. (55) reduces to the form derived previously.[10,13] It is remarkable that we can obtain the master equation valid for any time scale only by retaining the upper limit of the τ integrals appearing in the functions (52a)–(52d) to the finite value t.

5. CONCLUDING REMARKS

We have seen that our expression for the quantal master equation, in a form suitable for the application of perturbational treatment, is successfully applied to two examples, and that the essential features of the Kubo theory of the line shape can be incorporated into the framework of our theory. Some remarks are due with respect to the latter point.

First, we can integrate Eq. (12) by making use of a suitably chosen ordered exponential function, as

$$\rho(t) = \exp_{\leftarrow}\{-i(L_S + \langle L_{SB}\rangle_B)t - \int_0^t d\tau(t-\tau)\Phi(\tau)\}\rho(0) \tag{58}$$

where

$$\Phi(\tau) = \langle iL_{SB}\dot{\theta}(\tau)\rangle_B \tag{59}$$

We can see the analogy of this operator expression to the transition probability (38) with the coefficient (39) in the stochastic theory of Kubo. Thus we can discuss various results obtained either as a long-time approximation (narrowing limit) or as a short-time approximation in the same way as in the Kubo theory. The selection of time scale in which we are interested can be done more easily and more systematically by the method of time scaling. The latter method will be applied in a separate paper.

Next, if we want to generalize the stochastic Liouville equation due to Kubo in a straightforward way, we should rather introduce a *time-dependent* stochastic Hamiltonian instead of the explicit introduction of a heat reservoir. To do this, we have to modify our expression. This problem is connected with the one to be discussed below.

Finally, we should refer to the memory in the conventional damping-theoretical expression

$$\begin{aligned}\mathscr{P}\dot{W}(t) = &-i\mathscr{P}L\mathscr{P}W(t) - \int_0^t d\tau\mathscr{P}Le^{-i\mathscr{Q}L\tau}\mathscr{Q}L\mathscr{P}W(t-\tau) \\ &- i\mathscr{P}Le^{-i\mathscr{Q}Lt}\mathscr{Q}W(0)\end{aligned} \tag{60}$$

Comparing this expression with Eq. (4), we see that the latter expression can be obtained by transferring some part, i.e., $1 - \theta(t)$, of the last destruction term in the former into the memory term to cancel the memory effect. This condition is sufficient to determine the exact form of $\theta(t)$, Eq. (5) in the case of time-independent $\mathscr{H}$ and $\mathscr{P}$. This will be shown in subsequent papers, in which generalizations to the cases of a *time-dependent Hamiltonian* and of a *time-dependent projection operator* will also be done. These generalizations are necessary in dealing with various problems in physics.

In conclusion, as we have already referred to in Section 3, it should be emphasized that in practical applications there will be cases in which our memoryless form of the master equation gives improved approximate solutions compared to those given by the conventional form with memory. Equation (12), with the operator (13) or (23), and Eq. (26) are of course *both exact*, under the initial condition (14), and coincide with each other in the narrowing limit. But if we truncate the operator $\Psi(t)$ in our Eq. (12)

or the memory kernel in the conventional equation (26), the situation changes, and it may occur that these two approximate master equations, Eq. (12) with (25) and Eq. (27), give quite different solutions except in the narrowing limit. An important and frequently found example is a *localized system* under the influence of its surroundings, to which the present theory is mainly intended to apply, and for which the force produced by the surroundings and acting upon the system may be regarded as behaving like a *Gaussian process*. In the limit where the force is strictly a Gaussian process, *the lowest order equation*, i.e., Eq. (12) with (25), *will become exact*, whereas the corresponding equation (27) will be a poor approximation for an arbitrary time scale. In order to prove this statement we should take steps similar to proving the central limit theorem by assuming the force, or the interaction Hamiltonian $\mathscr{H}_{SB}$, composed of a large number of parts. This is an interesting and important problem in mathematical physics, but it will require sophisticated mathematical tools, such as those used by Davies *et al.*[15] to take the narrowing limit. Instead of doing the proof within the present formulation, we shall discuss Kubo's *stochastic model* of frequency modulation referred to in Section 3, for which all the equations concerned can be solved exactly. This will be done in our next paper, where we shall discuss the stochastic Liouville equation.

APPENDIX A. SHORT PROOF OF EQ. (4)

Introducing an operator $f(t)$ defined by

$$f(t) = \mathscr{P} + e^{-i\mathscr{Q}Lt}\mathscr{Q}e^{iLt} \tag{A.1}$$

and its inverse $\theta(t)$, we write the quantal Liouville equation as

$$\begin{aligned} \dot{W}(t) &= -iL\theta(t)f(t)W(t) \\ &= -iL\theta(t)\mathscr{P}W(t) - iL\theta(t)e^{-i\mathscr{Q}Lt}\mathscr{Q}W(0) \end{aligned} \tag{A.2}$$

where we have used

$$W(t) = e^{-iLt}W(0) \tag{A.3}$$

Separating the drift term $-iL\mathscr{P}W(t)$ from the first term in Eq. (A.2), we arrive at expression (4).

Making use of the identity

$$\theta(t) - 1 = \int_0^t d\tau \dot{\theta}(\tau) \tag{A.4}$$

and the relation

$$\begin{aligned} \dot{\theta}(\tau) &= \theta(\tau)\dot{f}(\tau)\theta(\tau) \\ &= -\theta(\tau)e^{-i\mathscr{Q}L\tau}i\mathscr{Q}Le^{iL\tau}\theta(\tau) \end{aligned} \tag{A.5}$$

we can transform Eq. (4) into the form proposed by Tokuyama and Mori.

It might be considered that the form of $f(t)$ or of $\theta(t)$ was arbitrarily taken, but this is not the case. As is discussed in the concluding remarks in the text, the form of $\theta(t)$ is determined uniquely by the damping theory.

APPENDIX B. PROOF OF EQS. (53) AND (54)

The *orbital angular momentum* is represented by

$$L_x = i\left(\sin\varphi\frac{\partial}{\partial\vartheta} + \cot\vartheta\cos\varphi\frac{\partial}{\partial\varphi}\right) \tag{B.1a}$$

$$L_y = i\left(-\cos\varphi\frac{\partial}{\partial\vartheta} + \cot\vartheta\sin\varphi\frac{\partial}{\partial\varphi}\right) \tag{B.1b}$$

and

$$L_z = -i\frac{\partial}{\partial\varphi} \tag{B.1c}$$

which can be rewritten by considering m_x and m_y as independent variables:

$$L_x = im_z\frac{\partial}{\partial m_y}, \qquad L_y = -im_z\frac{\partial}{\partial m_x} \tag{B.2a}$$

and

$$L_z = i\left(m_y\frac{\partial}{\partial m_x} - m_x\frac{\partial}{\partial m_y}\right) \tag{B.2b}$$

We see that

$$[L_\mu, L_\nu] = iL_\lambda, \qquad [m_\mu, L_\nu] = im_\lambda \tag{B.3}$$

provided that a set (λ, μ, ν) forms an even permutation of (x, y, z).

From Eqs. (B.2) we immediately prove that

$$\mathbf{L}\cdot\mathbf{m} = L_x m_x + L_y m_y + L_z m_z = 0 \tag{B.4a}$$

and

$$\mathbf{m}\cdot\mathbf{L} = m_x L_x + m_y L_y + m_z L_z = 0 \tag{B.4b}$$

Let us next consider the quantity $\mathbf{L}\cdot(\mathbf{m}\times\mathbf{L})$. This can be calculated as

$$\begin{aligned}\mathbf{L}\cdot(\mathbf{m}\times\mathbf{L}) &= L_x(m_yL_z - m_zL_y) + L_y(m_zL_x - m_xL_z) + L_z(m_xL_y - m_yL_x)\\ &= [m_xL_z, L_y] + [m_yL_x, L_z]\\ &\quad + [m_zL_y, L_x] + i(m_xL_x + m_yL_y + m_zL_z)\\ &= i\mathbf{m}\cdot\mathbf{L} = 0\end{aligned} \tag{B.5}$$

by virtue of Eqs. (B.3) and (B.4b). If we use Eqs. (B.4a) and (B.5), we find at once Eq. (54) for the expressions (50a) and (50b).

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