Statistical reduction for strongly driven simple quantum systems

S. Mukamel, I. Oppenheim, and John Ross
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 26 September 1977)

We derive reduced equations of motion for simple quantum systems which are strongly driven by an external field and are modulated stochastically by a coupling to a bath. In the derivation we make use of the cumulant-expansion method of Kubo using two different time-ordering prescriptions. We demonstrate how the choice of the ordering prescription is related to the statistical properties of the bath, once the cumulant expansion is truncated. Our equations of motion are valid for arbitrary time scale for the motions of the bath relative to those of the system, and they change smoothly from the static to the Markov (motional narrowing) limit. As examples, we consider the problems of a randomly modulated and driven harmonic oscillator and a modulated and damped two-level system. In the Markovian limit both ordering prescriptions yield Bloch-type equations of motion; in general, however, the driving and modulation interfere and the different statistical properties of the bath, as determined by the two truncated ordering prescriptions, lead to different results.

I. INTRODUCTION

The partial statistical description of physical processes requires the derivation of appropriate equations of motion (master equations) for a few relevant variables (coordinates, operators, density-matrix elements) which are called the system and which are correlated, hopefully weakly, to the remaining variables called the bath.[1-3]

The problem is much simplified when there exists a distinct time-scale separation between the motions of the system and those of the bath. When the characteristic time scale of the bath is much faster than that of the system (Markovian limit with no memory effects), it is possible to solve the bath problem by treating the system variables as parameters. Thereafter one solves a reduced set of system equations, assuming that the bath adjusts to the state of the system. In such a case many of the known techniques (projection operators in Liouville space, cumulant expansion, Langevin approach, etc.) yield relatively simple equations and such approaches are commonly used in various problems such as spin relaxation,[4] pressure broadening of line shapes,[5] semiclassical theories of chemical processes,[6] and quantum optics.[3]

In the other extreme, labeled static, where the bath is motionless it is possible to solve for the motion of the system for a given configuration of the bath and then average over the distribution of bath states. As an example of a static analysis consider any inhomogeneous broadening of line shapes,[7] for instance, Doppler broadening. Here, the translational degrees of freedom of the absorber are the bath. At low frequency of collisions the translational distribution is static and the line shape may be represented as a convolution of the Doppler-free line shape and the Gaussian distribution of molecular frequencies. This situation, however, changes when the time between collisions becomes sufficiently short compared to the time scale for the driving of the system.[7]

The time-scale separation is a powerful method where applicable. There are many problems, however, for which it may not be possible in general to define the variables in such a way that a time-scale separation is valid. Some of these are (i) line-shape theories in all spectral ranges (magnetic resonance, microwave, visible uv), either in the gas phase or in condensed phases[8,9]; (ii) resonance fluorescence and Raman spectroscopy including saturation and collisional effects[10]; (iii) multiphoton processes in large molecules[11]; (iv) theories of chemical reactions of polyatomic molecules[12]; and (v) atom-surface scattering.[13] In examples (i)–(iii) the system is typically a few atomic or molecular levels, interacting with the radiation field. The bath can be of various kinds, such as (a) other molecules which collide with the optically active molecule; (b) intramolecular interactions which couple the various molecular modes in large molecules; (c) electron-phonon interactions in impurity spectra[14]; (d) dipolar interactions in condensed phases.[8] In example (iv) we may choose for the system the few molecular modes which are strongly correlated with the reaction dynamics; the rest of the modes which perturb the dynamics are considered to be the bath. Finally, in example (v), the gas atom plus a few surface atoms may be chosen to be the system, and the rest of the solid provides the bath.

A sufficient condition for a partial statistical description to be useful is that the motions of the system and the bath are weakly correlated. If that is not the case, one should solve self-consistently for the system and the bath and the description becomes complicated, though feasible.[2] This condition of weak correlation is often valid when there is a time-scale separation, but it may hold even when the time scales are comparable, due to other reasons, for instance the presence of many degrees of freedom in the bath. There is the hope then that a simple description of the bath in terms of a few stochastic properties may be sufficient for a description of its effects on the system.

Kubo[8] has shown how to solve line-shape problems in principle without relying on a time-scale separation between the system and the bath, by invoking a perturbative treatment for the interaction of the system with the radiation field. The model considered by Kubo was a two-level system driven by a weak field. The two-level frequency was assumed to be randomly modulated by the interaction with the bath, and to undergo a stationary Gaussian process. The line-shape function derived by Kubo goes smoothly from a Gaussian in the static limit (slow motions of bath degrees of freedom) to a narrow Lorentzian in the Markovian limit for fast motion of the bath degrees of freedom, also called fast modulation, or the motional narrowing limit. Recently these treatments were extended and applied to second-order optical processes[15] (resonance fluorescence with weak excitation fields), again with the restriction of low-order perturbation theory for the field.

In this paper we make use of the cumulant expansion of Kubo to derive equations of motion for simple quantum systems (two-level system, harmonic oscillator) whose frequency undergoes a random modulation and which are driven by a strong field. In Sec. II we outline briefly the cumulant-expansion method.[8,16] Basically, this method enables us to derive closed equations of motion for a selected set of degrees of freedom which include a desired amount of information regarding the behavior of the bath. This information is expressed in terms of appropriate correlation functions which can be calculated with simple dynamical models for the bath. Alternatively, one can adopt a stochastic description of the bath. The cumulant-expansion method provides us with a large degree of flexibility, as we can adopt different time-ordering prescriptions. By carrying out the cumulant expansion to infinite order, the ordering becomes unimportant. However, once the cumulant expansion is truncated at some order, then the choice of the time ordering becomes crucial, as it implies different choices of statistical properties of the bath. Knowing the statistical properties of the bath, we should look for the time-ordering method most convenient to describe these properties.

In Sec. III we consider the problem of the randomly modulated and driven harmonic oscillator, using two different ordering prescriptions, the chronological-ordering prescription (COP) and a partial-ordering prescription (POP). In Sec. IV we treat the modulated and damped two-level system using the same techniques.

In the Markovian limit, both ordering prescriptions result in the same "Bloch-type" equations of motion. The effects of the bath may then be incorporated by including a relaxation time T_2 in the equations. In the general case, however, the driving and modulation interfere and the different statistical properties of the bath in the two ordering prescriptions lead to different solutions. The models considered here are of direct applicability to the physical problems (i)–(iii) above, but the method can be applied also to other problems [e.g., (iv), (v)].

II. REDUCED EQUATIONS OF MOTION

We consider a set of a few degrees of freedom (the system) coupled to other degrees of freedom (the bath). We are interested in deriving a closed set of equations of motion for the variables of the system.[3,4,8,16] The total Hamiltonian is

$$H=H_S+H_R+H'=H_0+H' , \tag{1}$$

where H_S, H_R, and H' denote the Hamiltonian of the system, of the bath, and the interaction between system and bath, respectively. We define the appropriate Liouville operators

$$\begin{aligned} &L=[H,\ ],\quad L_S=[H_S,\ ],\\ &L'=[H',\ ],\quad L_R=[H_R,\ ]. \end{aligned} \tag{2}$$

The total density matrix of the system plus the bath obeys the Liouville equation

$$\frac{\partial\rho}{\partial t}=-iL\rho . \tag{3}$$

We now change to the interaction representation,

$$\begin{aligned} &\tilde\rho(t)=e^{iL_0t}\rho=e^{iH_0t}\rho e^{-iH_0t} ,\\ &\tilde L'(t)=e^{iL_0t}(L-L_0)e^{-iL_0t}=[e^{iL_0t}(H-H_0),\ ], \end{aligned} \tag{4}$$

to obtain

$$\frac{\partial\tilde\rho}{\partial t}=-i\tilde L'\tilde\rho . \tag{5}$$

At time $t=0$ the system and bath are assumed to be uncorrelated, i.e.,

$$\tilde\rho(0)=\tilde\sigma(0)\tilde R(0) , \tag{6}$$

where $\tilde{\sigma}$ and $\tilde{R}$ are the system and bath density matrices, respectively,

$$\tilde{\sigma}=\langle\tilde{\rho}\rangle\equiv \mathrm{tr}_{\mathrm{bath}}\tilde{\rho}\,,\qquad \tilde{R}=\mathrm{tr}_{\mathrm{system}}\tilde{\rho}\,. \tag{7}$$

The formal solution for $\tilde{\sigma}(t)$ is

$$\tilde{\sigma}(t)=\langle\tilde{U}(t,0)\rangle\tilde{\sigma}(0)\,, \tag{8}$$

where

$$\tilde{U}(t,0)=1+\sum_{n=1}^{\infty}M_n(t)\,, \tag{9}$$

$$M_n(t)=i^n\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{n-1}}d\tau_n \times m_n(\tau_1,\tau_2,\ldots,\tau_n) \tag{10a}$$

$$m_n(\tau_1,\tau_2,\ldots,\tau_n)=\langle\tilde{L}'(\tau_1)\tilde{L}'(\tau_2)\cdots\tilde{L}'(\tau_n)\rangle \equiv \mathrm{tr}_{\mathrm{bath}}[\tilde{L}'(\tau_1)\tilde{L}'(\tau_2)\cdots\tilde{L}'(\tau_n)]\,. \tag{10b}$$

Equations (8) and (9) provide an expansion of $\tilde{\sigma}(t)$ in the moments M_n of the evolution operator $\langle\tilde{U}\rangle$. We now make use of the cumulant expansion of Kubo[16] to rewrite $\langle\tilde{U}\rangle$ in the form

$$\langle\tilde{U}(t,0)\rangle\equiv \exp_P K(t)\,, \tag{11a}$$

where

$$K(t)=\sum_{n=1}^{\infty}K_n(t)\,. \tag{11b}$$

Each K_n is a cumulant or connected average defined in terms of $m_1,\ m_2,\ldots,m_n$; P is an ordering prescription. The flexibility of this formulation lies in our freedom to choose P in many different ways and then to define the appropriate cumulants K_n so as to satisfy Eq. (11a). Of course, any *infinite*-order cumulant expansion gives the same result. However, it is often convenient to consider Gaussian processes (in which all cumulants of order >2 vanish). Then it becomes important to choose the right ordering for a particular problem.

We adopt here two different time-ordering prescriptions. (i) A partial ordering prescription (POP)[16,4(b)] is designed to construct equations of motion of the form

$$\frac{\partial\tilde{\sigma}(t)}{\partial t}=\sum_{n=1}^{\infty}\dot{K}_n(t)\tilde{\sigma}(t)\,, \tag{12a}$$

where

$$\dot{K}_n(t)=\frac{d}{dt}K_n(t)\,. \tag{12b}$$

If we choose L_0 so that $\langle L'\rangle=0$, we then have

$$K_1=0\,,\quad K_2=M_2\,,\quad K_3=M_3\,,$$

$$K_4=M_4-\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\int_0^{\tau_3}d\tau_4[m_2(\tau_1,\tau_2)m_2(\tau_3,\tau_4)+m_2(\tau_1,\tau_3)m_2(\tau_2,\tau_4)+m_2(\tau_1,\tau_4)m_2(\tau_2,\tau_3)]\,, \tag{13}$$

and transforming back to the Schrödinger picture for the system operators we get

$$\frac{\partial\sigma}{\partial t}=-iL_s\sigma+e^{-iL_st}\sum_{n=1}^{\infty}\dot{K}_n(t)e^{iL_st}\sigma(t)\,. \tag{14}$$

To second order Eq. (14) assumes the form

$$\frac{\partial\sigma}{\partial t}=-iL_s\sigma-\left(\int_0^t d\tau\langle L_1(t)e^{-iL_s\tau}L_1(t-\tau)e^{iL_s\tau}\rangle\right)\sigma\,, \tag{15}$$

where

$$L_1(\tau)=e^{iL_R\tau}L'e^{-iL_R\tau}\,. \tag{16}$$

(ii) Another choice of time ordering is the chronological ordering prescription (COP), resulting in the following reduced equations of motion for $\tilde{\sigma}$:

$$\frac{\partial\tilde{\sigma}}{\partial t}=\sum_{n=1}^{\infty}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{n-1}}d\tau_n\,\theta_{n+1}(t,\tau_1,\ldots,\tau_n)\tilde{\sigma}(\tau_n)\,, \tag{17}$$

where

$$\theta_1=0\,,\quad \theta_2=m_2\,,\quad \theta_3=m_3\,,\quad \theta_4(\tau_1,\tau_2,\tau_3,\tau_4)=m_4-m_2(\tau_1,\tau_2)m_2(\tau_3,\tau_4)\,, \tag{18}$$

and in the Schrödinger picture

$$\frac{\partial\sigma}{\partial t} = -iL_s\sigma + \sum_{n=1}^{\infty}\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{n-1}} d\tau_n e^{-iL_s t}\theta_{n+1}(t,\tau_1,\ldots,\tau_n)e^{iL_s\tau_n}\sigma(\tau_n)\,. \tag{19}$$

To second order Eq. (19) becomes

$$\frac{\partial\sigma}{\partial t} = -iL_s\sigma - \int_0^t d\tau\langle L_1(t)e^{-iL_s(t-\tau)}L_1(\tau)\rangle\sigma(\tau)\,. \tag{20}$$

We recall here that the COP expressions are identical to the results obtained by using Fano-Zwanzig-Mori[1,17,18] projection operators in Liouville space. They arise naturally, as the usual formal solution of the Liouville equation contains only chronologically ordered operators. The POP arises from resummation of the COP expressions; it leads to a simpler differential equation [(14) rather than (19)] and it enables us to treat more conveniently various types of statistical approximations to the motion of bath degrees of freedom. Going to nth order in the POP cumulant expansion is equivalent to assuming that all the cumulants K_{n+1}, $K_{n+2}, \ldots$ are zero. This results in expressing all the moments higher than the nth in terms of the n first moments [see Eq. (13)]. On the other hand, an nth-order description using the COP implies that $\theta_{n+1}, \theta_{n+2}, \ldots$ [Eq. (18)] vanish. This amounts to assuming different statistical properties of the bath. Thus the appropriate expansion should be adopted for the problem at hand. This issue is discussed in Secs. III and IV, where we compare the results for simple model systems using Eqs. (15) and (20).

III. RANDOM FREQUENCY MODULATION OF A DRIVEN HARMONIC OSCILLATOR

We now present a model which is of interest to the problem of multiphoton molecular excitations in the infrared.[11] Various molecules (e.g., SF_6, $BCl_3, \ldots$) can absorb many (30–40) quanta of a high-power CO_2 laser (power densities of MW/cm^2) and dissociate under collision-free conditions. This process is of interest as a possible way of inducing laser-specific chemistry, and as a tool for investigating intramolecular interactions and reaction-rate theories. The basic molecular model[19] is that of a molecule having one active mode quasiresonant with a strong ir electromagnetic field. In order to be able to evaluate the amount of energy absorbed by the molecule and its distribution among the molecules subject to a given laser pulse, the following points should be considered: (i) the states prepared by the radiation field are not molecular eigenstates; (ii) the density of molecular states is a rapidly increasing function of energy. As a result of these facts, the radiatively active molecular states are being perturbed in the course of the molecular driving by the rest of the states. The effects of these perturbations may be classified into two categories: (a) First, there are dephasing (T_2) effects due to the random force exerted on the active states, which do not bring about relaxation of the active states. These perturbations destroy the coherent nature of the molecular driving and broaden the molecular levels, which results in a decrease in the multiphoton absorption cross section. T_2 is expected to be of the order of the spread in the molecular frequencies, which is the time required for various components to become out of phase. (b) Second, there occur T_1 processes, involving relaxation of the energy into the other modes. The dephasing effects are expected to be dominant in the broadening, and they affect the amount of energy absorbed as well as the distribution of energy among different molecules. The T_1 processes, on the other hand, determine the distribution of energy within the molecule among the various modes.

In the present model we address ourselves to the dephasing problem. We thus assume that (i) we have an active molecular mode which is taken to be a harmonic oscillator; this mode and the radiation field are the system; and (ii) the rest of the molecular states (other than the active mode) are the bath degrees of freedom and are assumed to modulate stochastically the frequency of the active oscillator. Classically the bath may be viewed as a collection of oscillators, with random initial phases, exerting a random force on a selected oscillator. The effect of the bath on the system is taken into account by letting the oscillator frequency ω be a random process with characteristic variance δ and correlation time Γ^{-1}, i.e.,

$$\omega = \omega_0 + \delta\omega\,, \tag{21a}$$

$$\langle\omega\rangle = \omega_0\,, \tag{21b}$$

and

$$\langle\delta\omega(t)\delta\omega(0)\rangle = g^2 e^{-\Gamma|t|}\,. \tag{21c}$$

The absorption line shape of the oscillator for this model has been calculated for a weakly driving electromagnetic field by Kubo[8], who assumed that the stationary distribution of the stochastic variable $\delta\omega$ is a Gaussian. When the bath motions are infinitely slow ($\Gamma \ll g$ static limit), the absorption spectrum just reflects the frequency distribution of the oscillator and is a Gaussian of width g. However, in the Markovian limit $\Gamma \gg g$ the motional narrowing condition is obeyed and the spectrum becomes a Lorentzian with characteristic width g^2/Γ. We now solve this problem for arbitrary field strength and for arbitrary time scales of the bath.

Denoting by $a^\dagger$ (a) the creation (annihilation) operators for the oscillator, we have for its Hamiltonian[3]

$$H = \omega_0 a^\dagger a + \delta\omega(t) a^\dagger a + 2\Omega \cos\omega_L t (a + a^\dagger) , \tag{22}$$

where ω_L, close to ω_0, is the frequency of an external driving field. The Heisenberg equations for motion for a and $a^\dagger a$ are

$$\frac{da}{dt} = -i(\omega_0 + \delta\omega)a - 2i\Omega \cos\omega_L t ,$$
$$\frac{da^\dagger a}{dt} = -4\Omega \mathrm{Im} \cos\omega_L t a . \tag{23}$$

We can now invoke the rotating-wave approximation (RWA)[3] which implies neglecting highly oscillatory terms $[\exp(\pm 2i\omega_L t)]$ in the equations. These terms do not contribute to the time evolution as long as $\Omega \ll \omega_L$. Denoting

$$\tilde{a} = a e^{i\omega_L t} , \tag{24}$$

we get

$$\frac{d\tilde{a}}{dt} = -i\Delta\tilde{a} - i\delta\omega\tilde{a} - i\Omega , \tag{25}$$

$$\frac{da^\dagger a}{dt} = -2\Omega \mathrm{Im}\tilde{a} , \tag{26}$$

$$\Delta = \omega_0 - \omega_L . \tag{27}$$

Using the formulation presented in Sec. II, we proceed to derive equations of motion for the quantities $\langle a\rangle$, $\langle a^\dagger a\rangle$, where $\langle\cdots\rangle$ denotes averaging over the stochastic part. The quantity which is of interest to us is the rate of energy absorption by the oscillator which is

$$\frac{d\langle E\rangle}{dt} = \frac{d\langle a^\dagger a\rangle}{dt} = -2\Omega \mathrm{Im}\langle\tilde{a}\rangle . \tag{28}$$

The algebraic manipulations are carried out in Appendix A. We give only the final results for $d\langle a\rangle/dt$. Using first the partial time-ordering method, we have

$$\frac{d\langle a\rangle}{dt} = [-i\Delta - \gamma_1(t)]\langle a\rangle - \gamma_2(t) - i\Omega , \tag{29a}$$

where

$$\gamma_i(t) = \int_0^t d\tau \langle \delta\omega(t)\delta\omega(t-\tau)\rangle \phi_i(\tau) , \tag{29b}$$

$$\phi_1(\tau) = [\Delta^2 + 2\Omega^2(1 + \cos\alpha\tau)]/\alpha^2 , \tag{29c}$$

$$\phi_2(\tau) = -\Omega(\Delta - \Delta\cos\alpha\tau + i\alpha\sin\alpha\tau)/\alpha^2 , \tag{29d}$$

and where

$$\alpha^2 = \Delta^2 + 4\Omega^2 . \tag{29e}$$

Substituting (29c), (29d), and (21c) in (29b) and integrating we obtain the results

$$\gamma_1(t) = \frac{g^2}{\Gamma}\left(\frac{\Delta^2 + 2\Omega^2}{\alpha^2}(1 - e^{-\Gamma t}) + \frac{2\Omega^2}{\alpha^2} F_1(t)\right) , \tag{30a}$$

$$\gamma_2(t) = \frac{g^2\Omega}{\Gamma\alpha}\left(\frac{\Delta}{\alpha}(1 - e^{-\Gamma t}) - \frac{\Delta}{\alpha} F_1(t) + iF_2(t)\right) , \tag{30b}$$

$$F_1(t) = \Gamma \int_0^t d\tau\, e^{-\Gamma\tau} \cos\alpha\tau$$
$$= \Gamma \frac{\Gamma(1 - \cos\alpha t e^{-\Gamma t}) + \alpha \sin\alpha t e^{-\Gamma t}}{\alpha^2 + \Gamma^2} , \tag{30c}$$

$$F_2(t) = \Gamma \int_0^t d\tau\, e^{-\Gamma\tau} \sin\alpha\tau$$
$$= \Gamma \frac{\alpha(1 - e^{-\Gamma t}\cos\alpha t) - \Gamma \sin\alpha t e^{-\Gamma t}}{\alpha^2 + \Gamma^2} . \tag{30d}$$

The solution of Eq. (29a) is

$$\langle a\rangle = e^{-i\Delta t} \exp\left(-\int_0^t d\tau\, \gamma_1(\tau)\right)\langle a(0)\rangle$$
$$- \int_0^t d\tau' [\gamma_2(\tau') + i\Omega] \exp[-i\Delta(t - \tau')]$$
$$\times \exp\left(-\int_{\tau'}^t \gamma_1(\tau)\, d\tau\right) . \tag{31}$$

If, however, we use the chronological time ordering, we get (see Appendix A)

$$\frac{d\langle a\rangle}{dt} = -i\Delta\langle a\rangle - i\Omega - \int_0^t d\tau \langle\delta\omega(t)\delta\omega(\tau)\rangle$$
$$\times \hat{\phi}(t-\tau)\langle a(\tau)\rangle , \tag{32a}$$

where

$$\hat{\phi}(t-\tau) = \frac{\Delta + \alpha}{2\alpha} \exp\left(-i\frac{\Delta + \alpha}{2}(t - \tau)\right)$$
$$- \frac{\Delta - \alpha}{2\alpha} \exp\left(-i\frac{\Delta - \alpha}{2}(t - \tau)\right)$$
$$\equiv \hat{\phi}_+(t-\tau) - \hat{\phi}_-(t-\tau) . \tag{32b}$$

The COP integro-differential equation (32a) may be converted to a system of ordinary linear differential equations with the substitution

$$\langle m\rangle = g^2 \int_0^t d\tau\, e^{-\Gamma(t-\tau)} \hat{\phi}_+(t-\tau)\langle a(\tau)\rangle ,$$
$$\langle n\rangle = g^2 \int_0^t d\tau\, e^{-\Gamma(t-\tau)} \hat{\phi}_-(t-\tau)\langle a(\tau)\rangle , \tag{33}$$

and we have

$$\frac{d\langle a\rangle}{dt} = -i\Delta\langle a\rangle - \langle m\rangle + \langle n\rangle - i\Omega\,,$$

$$\frac{d\langle m\rangle}{dt} = g^2\frac{\Delta+\alpha}{2\alpha}\langle a\rangle - \left(\Gamma + i\frac{\Delta+\alpha}{2}\right)\langle m\rangle\,, \qquad (34a)$$

$$\frac{d\langle n\rangle}{dt} = -g^2\frac{\Delta-\alpha}{2\alpha}\langle a\rangle - \left(\Gamma + i\frac{\Delta-\alpha}{2}\right)\langle n\rangle\,.$$

Equations (34a) can be solved with standard techniques with the initial conditions

$$\langle a(0)\rangle = a_0\,,\quad \langle m(0)\rangle = \langle n(0)\rangle = 0\,. \qquad (34b)$$

Our general results, i.e., Eq. (31) and the solutions of (34a), can be substituted into Eq. (28) to give the rate of energy absorption by the oscillator from the field. Let us consider now several limiting cases.

(i) *The Markovian limit* (i.e., *fast-modulation or motional-narrowing limit*). In this limit the bath is assumed to have an extremely short correlation time, much shorter than any time scale of the system, i.e., $\Gamma \gg g, \alpha$ (g^2/Γ finite). For this condition, one can carry the integrations in Eq. (29b) to infinity, which implies no change of the system during the correlation time. In the POP we get

$$\gamma_1 \to \int_0^\infty d\tau\,\langle \delta\omega(t)\delta\omega(t-\tau)\rangle\,,\quad \gamma_2 \to 0\,, \qquad (35)$$

whereas in the COP we have

$$\hat{\phi} \to 1\,, \qquad (36)$$

and

$$\int_0^t d\tau\,\langle\delta\omega(t)\delta\omega(\tau)\rangle\langle a(\tau)\rangle \to \left(\int_0^\infty d\tau\,\langle\delta\omega(t)\delta\omega(t-\tau)\rangle\right)\langle a(t)\rangle\,. \qquad (37)$$

Thus, in this limit, both the COP and POP equations of motion reduce to the form

$$\frac{d\langle a\rangle}{dt} = -i\Delta\langle a\rangle - \hat{\Gamma}\langle a\rangle - i\Omega\langle a\rangle\,, \qquad (38)$$

where

$$\hat{\Gamma} = \int_0^\infty d\tau\,\langle\delta\omega(t)\delta\omega(t-\tau)\rangle\,, \qquad (39)$$

and for the particular form (21c) we get

$$\hat{\Gamma} = g^2/\Gamma\,. \qquad (40)$$

Equation (38) contains a dephasing term $-\hat{\Gamma}\langle a\rangle$ which is the net result of the rapid-frequency fluctuations. Thus we find that in this limit the equation of motion contains additive terms of driving and dephasing. The reason for the additivity is that the bath motions are so rapid that no significant driving occurs during the correlation time of the bath motion and thus the damping term is not affected by the driving.[10(c)]

The solution for the line shape is in this case

$$\langle a\rangle = -i\Omega\int_0^t d\tau'\exp[-i\Delta(t-\tau')]\times\exp[-(g^2/\Gamma)(t-\tau')]\,,$$

$$\langle a\rangle = i\Omega\frac{\exp[(-i\Delta - g^2/\Gamma)t] - 1}{i\Delta + g^2/\Gamma} \xrightarrow[t\to\infty]{} -i\Omega/(i\Delta + g^2/\Gamma)\,, \qquad (41)$$

$$\frac{d\langle E\rangle}{dt} = -2\Omega\,\mathrm{Im}\langle a\rangle \xrightarrow[t\to\infty]{} 2\Omega^2\frac{g^2/\Gamma}{\Delta^2 + (g^2/\Gamma)^2}\,. \qquad (42)$$

We see that in this limit the line shape becomes Lorentzian and that no saturation is observed (i.e., the rate of energy absorption is always proportional to the light intensity Ω^2).

(ii) *The line shape in a weak driving field.* In order to get an expression for the line shape in a weak driving field, we have to solve for $\langle a\rangle$ to lowest order in Ω. In addition, we have to switch the field adiabatically. We shall thus use the following linear-response expression for the line shape[8]:

$$I(\Delta) = \int_0^\infty d\tau\,\cos\Delta\tau\,\frac{\langle a(\tau)a(0)\rangle}{\langle a(0)^2\rangle}\,, \qquad (43)$$

where

$$\langle a(\tau)a(0)\rangle/\langle a(0)^2\rangle$$

is the zero-field correlation function for the polarization in the interaction representation. It is obtained as the solution for $\langle a\rangle$ [Eq. (29) or (34)] by setting $\Omega = 0$, $\Delta = 0$, $\langle a(0)\rangle = 1$.

Using the POP we get

$$\left(\frac{\langle a(\tau)a(0)\rangle}{\langle a(0)^2\rangle}\right)_{\mathrm{POP}} = \exp\left(-\int_0^\tau d\tau_1\,\gamma_1(\tau_1)\right) = \exp\left(-\frac{g^2}{\Gamma^2}(e^{-\Gamma\tau} + \Gamma\tau - 1)\right)\,. \qquad (44)$$

Substitution of (44) in (43) results in

$$I(\Delta) = \int_0^\infty d\tau\,\cos\Delta\tau\,\exp\left(-\frac{g^2}{\Gamma^2}(e^{-\Gamma\tau} + \Gamma\tau - 1)\right). \qquad (45)$$

Equation (45) reduces in the Markovian limit $\Gamma \gg g, \Omega$ to the Lorentzian [Eq. (42)], whereas in the reverse, static limit (or slow modulation, $\Gamma \ll g$) we get

$$I(\Delta) = \int_0^\infty d\tau\,\cos\Delta\tau\,e^{-g^2\tau^2/2} = \tfrac{1}{2}(2\pi/g^2)^{1/2}e^{-\Delta^2/2g^2}\,. \qquad (46)$$

Turning now to the COP, we have, setting $\Omega = 0$, $\Delta = 0$ in Eq. (34a),

$$\frac{d\langle a\rangle}{dt} = -\langle m\rangle\,,\quad \frac{d\langle m\rangle}{dt} = g^2\langle a\rangle - \Gamma\langle m\rangle\,, \tag{47}$$

or alternatively

$$\langle\ddot{a}\rangle + \Gamma\langle\dot{a}\rangle + g^2\langle a\rangle = 0\,. \tag{48}$$

The solution of Eq. (48) with the initial conditions $\langle a(0)\rangle = a_0$, $\langle\dot{a}(0)\rangle = 0$ is

$$\langle a\rangle = \frac{a_0}{\lambda_+ - \lambda_-}(\lambda_+ e^{\lambda_- t} - \lambda_- e^{\lambda_+ t})\,, \tag{49a}$$

where

$$\lambda_\pm = \tfrac{1}{2}[-\Gamma \pm (\Gamma^2 - 4g^2)^{1/2}]\,. \tag{49b}$$

Thus

$$\left(\frac{\langle a(t)a(0)\rangle}{\langle a(0)\rangle^2}\right)_{\rm COP} = \frac{\lambda_+ e^{\lambda_- t} - \lambda_- e^{\lambda_+ t}}{\lambda_+ - \lambda_-}\,. \tag{50}$$

As for the line shape, in the Markovian limit $\Gamma \gg \delta$ we have

$$\left(\frac{\langle a(\tau)a(0)\rangle}{\langle a(0)^2\rangle}\right)_{\rm COP} = e^{-(g^2/\Gamma)t}\,, \tag{51}$$

and the line shape is again Lorentzian (same as POP). In the other limit, $g \gg \Gamma$, the line shape becomes oscillatory

$$\lambda_\pm = \tfrac{1}{2}(-\Gamma \pm 2ig)\,, \tag{52}$$

$$\left(\frac{\langle a(\tau)a(0)\rangle}{\langle a(0)^2\rangle}\right)_{\rm COP} = \frac{1}{g}\, e^{-\Gamma\tau/2}(\tfrac{1}{2}\Gamma \sin g\tau + g\cos g\tau)\,, \tag{53}$$

$$I(\Delta) = \frac{1}{g}\int_0^\infty d\tau\, e^{-\Gamma\tau/2}(\tfrac{1}{2}\Gamma \sin g\tau \cos\Delta\tau + g\cos g\tau \cos\Delta\tau)\,. \tag{54}$$

We note that the two correlation functions (44) and (50) show very different behavior. In the narrowing limit $\Gamma \gg g$ they both reduce to exponential behavior, varying as $\exp[-(g^2/\Gamma)t]$ for COP and POP. However, the POP goes smoothly into a Gaussian, $\exp\{-g^2t^2\}$, in the static limit ($\Gamma \ll g$), whereas the COP correlation function becomes oscillatory (as $\lambda_\pm$ becomes complex) when $g > \Gamma$. This difference is due to the fact that the two "Gaussian" processes defined by COP and POP are different. In fact, they have the same first three moments but from there on they differ.

A "COP Gaussian" has the property

$$m_{2n} = (m_2)^n\,. \tag{55}$$

A "POP Gaussian" has a Gaussian singlet distribution

$$P^{(1)}(\omega) \sim \exp(-\omega^2/g^2)\,. \tag{56}$$

From this example we see that we can introduce a variety of different "Gaussian processes" by truncating the various types of cumulant expansions, corresponding to different time ordering, at second order. If we want the Gaussian process to have a Gaussian stationary distribution, then we must use the POP. This point clarifies a recent attempt by Tokuyama and Mori[20] to establish the relation between the Zwanzig-Mori-Fano[1,17,18] formulation and the frequency modulations of Kubo. Tokuyama and Mori started from an equation of motion of the form (19) (with memory) and inverted it to obtain an equation which looked formally like (12). However, their expressions for K_n involve the operators $\langle\tilde{U}\rangle$ and $\langle\tilde{U}\rangle^{-1}$, which require knowledge of the full dynamics. Our analysis shows that the operators of Mori and the line-shape formulation of Kubo correspond simply to the COP and POP of the same cumulant expansion, and Eqs. (13) and (18) provide a simple comparison of the operators in both cases.

(iii) *Line shape in the sudden limit.* Another interesting limit is one in which the field is weak ($\Omega \ll \Delta$) and we are applying a pulse (sudden rather than adiabatic switching). In this case we get, using the POP, by expanding (29a) to lowest order in Ω,

$$\frac{d\langle a\rangle}{dt} = \left(-i\Delta - \frac{g^2}{\Gamma}(1 - e^{-\Gamma t})\right)\langle a\rangle - i\Omega\,. \tag{57a}$$

The term $1 - e^{-\Gamma t}$ switches on the damping so that if $\Gamma \gg \Omega, \Delta$, we again get the Lorentzian line shape; but when Γ is comparable to Δ, Ω the line shape is modified. In the COP we obtain, by expanding (34a) to lowest order in Ω

$$\frac{d\langle a\rangle}{dt} = -i\Delta\langle a\rangle - \langle m\rangle - i\Omega\,,\qquad \frac{d\langle m\rangle}{dt} = g^2\langle a\rangle - (\Gamma + i\Delta)\langle m\rangle\,, \tag{57b}$$

or

$$\langle\ddot{a}\rangle + (\Gamma + 2i\Delta)\langle\dot{a}\rangle + (i\Delta\Gamma + g^2 - \Delta^2)\langle a\rangle = 0\,. \tag{58}$$

In concluding this section we note that we have been able to derive and solve equations of motion for a driven harmonic oscillator in a strong electromagnetic field whose frequency undergoes a stationary Gaussian process, by using two time-ordering methods, COP and POP, in the cumulant expansion. In the weak-field limit we regain the expression of Kubo. We note that in the narrowing limit the absorption is proportional to the field intensity and no nonlinear effects in the field are found. The solution for the case of bath correlation time comparable to that of the system contains, however, nonlinear terms. This is reasonable: the fluctuations in the molecular levels destroy the harmonic nature of the oscillator when these fluctuations are on a time scale comparable to that of the electromagnetic driving field (part of the system).

IV. RANDOM MODULATION OF A DRIVEN TWO-LEVEL SYSTEM

The driven two-level system is a basic model in quantum optics.[3] The line-shape problem in the Markovian limit has been treated by Karplus and Schwinger[21] and van Vleck and Weisskopf.[22] The basic feature in which the solution differs from the previous one of the harmonic oscillator is in the appearance of saturation. The solution of this model for perturbations with arbitrary time scale is of interest for line-shape problems,[3,4,8] pressure broadening,[5] radiative collisions,[23] and multiphoton processes.[19] The Hamiltonian is[3]

$$H=E_a|a\rangle\langle a|+E_b|b\rangle\langle b|+\delta\omega(t)|b\rangle\langle b| + 2\Omega\cos\omega_L t(|a\rangle\langle b|+|b\rangle\langle a|)\,, \tag{59}$$

where E_a and E_b are the energies of the two states $|a\rangle$ and $|b\rangle$; $\delta\omega(t)$ is a stochastic random variable. In the rotating-wave approximation, the equations of motion for the density matrix are[3]

$$\begin{aligned}\frac{d}{dt}\rho_z&=-2i\Omega(\tilde\rho_{ab}-\tilde\rho_{ba})\,,\\ \frac{d}{dt}\tilde\rho_{ab}&=-i\Omega\rho_z-i\Delta\tilde\rho_{ab}-i\delta\omega(t)\tilde\rho_{ab}\,,\\ \frac{d}{dt}\tilde\rho_{ba}&=i\Omega\rho_z+i\Delta\tilde\rho_{ba}+i\delta\omega(t)\tilde\rho_{ba}\,,\end{aligned} \tag{60a}$$

where

$$\begin{aligned}&\rho_z=\rho_{aa}-\rho_{bb}\,,\quad \tilde\rho_{ab}=\rho_{ab}\exp(-i\omega_L t)\,,\\ &\tilde\rho_{ba}=\rho_{ba}\exp(i\omega_L t)\,,\quad \Delta=\omega_L-(E_b-E_a)\,.\end{aligned} \tag{60b}$$

In Appendix B we carry out the algebraic manipulations for obtaining the equations of motion for the reduced-density matrix. When we use the POP ordering the result is

$$\frac{d}{dt}\vec\sigma=-iA_0\vec\sigma-\Gamma(t)\vec\sigma\,, \tag{61a}$$

where

$$A_0=\begin{bmatrix}0 & -2i\Omega & 2i\Omega\\ -i\Omega & -i\Delta & 0\\ i\Omega & 0 & i\Delta\end{bmatrix}, \tag{61b}$$

$$\Gamma=\begin{bmatrix}0&0&0\\ \gamma_2(t)&\gamma_1(t)&0\\ \gamma_2^*(t)&0&\gamma_1(t)\end{bmatrix}, \tag{61c}$$

$$\gamma_i(t)=\int_0^t d\tau\,\langle\delta\omega(\tau)\delta\omega(0)\rangle\phi_i(\tau)\,, \tag{61d}$$

and

$$\begin{aligned}\phi_1(\tau)&=(\Delta^2+4\Omega^2\cos\alpha\tau)/\alpha^2\,,\\ \phi_2(\tau)&=\frac{\Omega\Delta}{\alpha^2}(1-\cos\alpha\tau)+i\,\frac{\Omega}{\alpha}\sin\alpha\tau\,.\end{aligned} \tag{61e}$$

$\vec\sigma$ is a column vector whose three components are $\sigma_{aa}-\sigma_{bb}$, σ_{ab}, and σ_{ba}. Assuming

$$\langle\delta\omega(t)\delta\omega(t-\tau)\rangle=g^2e^{-\Gamma\tau}\,, \tag{62}$$

we get

$$\begin{aligned}\gamma_1(\tau)&=\left(\frac{\Delta^2}{\alpha^2}(1-e^{-\Gamma\tau})+\frac{4\Omega^2}{\alpha^2}F_1(\tau)\right)\frac{g^2}{\Gamma}\,,\\ \gamma_2(\tau)&=\left(\frac{\Omega\Delta}{\alpha^2}(1-e^{-\Gamma\tau})-\frac{\Omega\Delta}{\alpha^2}F_1(\tau)+i\,\frac{\Omega}{\alpha}F_2(\tau)\right)\frac{g^2}{\Gamma}\,,\end{aligned} \tag{63}$$

where $F_1(\tau)$ and $F_2(\tau)$ were defined in Eqs. (30c) and (30d).

Turning now to the COP, we get the following reduced equation of motion (see Appendix B):

$$\frac{d\vec\sigma}{dt}=-iA_0\vec\sigma-g^2\int_0^t d\tau\,\hat\phi(t-\tau)\sigma(\tau)e^{-\Gamma(t-\tau)}\,, \tag{64a}$$

where

$$\hat\phi(t-\tau)=\begin{bmatrix}0&0&0\\ 0&\hat\gamma_1(t-\tau)&\hat\gamma_2(t-\tau)\\ 0&\hat\gamma_2(t-\tau)&\hat\gamma_1^*(t-\tau)\end{bmatrix}, \tag{64b}$$

$$\begin{aligned}\hat\gamma_1(t-\tau)&=\frac{4\Delta^2\cos\Delta(t-\tau)+8\Omega^2[1+\cos\Delta(t-\tau)]}{\Delta^2+4\Omega^2}\\ &\quad-2i\frac{\Delta}{\alpha}\sin\Delta(t-\tau)\,,\\ \hat\gamma_2(t-\tau)&=(8\Omega^2/\alpha^2)[\cos\Delta(t-\tau)-1]\,.\end{aligned} \tag{64c}$$

We make the following remarks regarding these results: (i) In the narrowing limit $\Gamma\gg g,\Omega$ both the POP and COP results reduce to the Bloch equations:

$$\frac{d\vec\sigma}{dt}=-iA_0\vec\sigma-\Gamma\vec\sigma\,, \tag{65a}$$

where

$$\Gamma=\begin{bmatrix}0&0&0\\ 0&\Gamma_2&0\\ 0&0&\Gamma_2\end{bmatrix}, \tag{65b}$$

and where

$$\Gamma_2=\int_0^\infty\langle\delta\omega(t)\delta\omega(t-\tau)\rangle d\tau=\frac{g^2}{\Gamma}\,. \tag{65c}$$

(ii) In the weak-field limit the line shape for this model coincides with that of the harmonic oscillator. (iii) In the general case (strong field, non-Markovian) we have to solve numerically Eqs.

(61a) or (64a) to get the line shape. (iv) The POP and COP correspond here to different statistical properties of the bath, as was discussed in detail in Sec. III.

V. CONCLUDING REMARKS

In this paper we have studied the role of the choice of the ordering prescription in the derivation of master equations for strongly driven quantum systems. The general way to proceed in actual problems is as follows: we start with a stochastic equation for the system of interest in which some part of the Hamiltonian is taken to be randomly fluctuating (due to the degrees of freedom of the bath which we do not consider explicitly). The statistical properties of the randomly fluctuating (stochastic) part (i.e., its correlation functions) should be evaluated with some simple model for the bath. The examples considered here (namely, random frequency shifts which behave as a stationary Gaussian process) were first used in magnetic resonance by Anderson and Weiss[24] to interpret the motional narrowing in liquids observed by Bloembergen, Purcell, and Pound.[25] In these systems, it is reasonable to assume a Gaussian random process for $\delta\omega$ since the frequency shifts $\delta\omega$ due to dipolar interactions are sums of many small contributions from all neighbors.

In the derivation of the master equation for this problem, if we were to use the COP, we must take the cumulant expansion [Eq. (19)] to infinite order as none of the θ_n vanish. However, using the POP [Eq. (12)], we have $K_n=0$, $n\geq 3$ for this model and thus a second-order cumulant expansion is sufficient. In general, for Gaussian processes, if the pertinent time-dependent bath quantities coupling to the system are functions (e.g., momentum) of commuting operators, we should use the POP; if the bath quantities are noncommuting operators (e.g., angular momentum) we should use COP.

The two models considered here demonstrate how to solve a problem of a strongly driven system coupled to a bath with arbitrary time scale. The models are of direct interest for the problems of line shapes and multiphoton molecular processes where intramolecular perturbations play an important role. The method used here and the comparison of the two ordering prescriptions may be of use for a variety of other quantum statistical problems which have common formal features.

ACKNOWLEDGMENT

This research was supported in part by the National Science Foundation and the Energy Research and Development Administration.

APPENDIX A: DERIVATION OF THE EQUATIONS OF MOTION FOR THE HARMONIC OSCILLATOR

Equation (25) is inhomogeneous. Let us first introduce a second variable $\tilde{b}(t)=1$ and rewrite it as

$$\frac{d}{dt}\begin{bmatrix}\tilde{a}\\ \tilde{b}\end{bmatrix} = -iA_0\begin{bmatrix}\tilde{a}\\ \tilde{b}\end{bmatrix} - iA'\begin{bmatrix}\tilde{a}\\ \tilde{b}\end{bmatrix}, \tag{A1}$$

where

$$A_0=\begin{bmatrix}\Delta & \Omega\\ 0 & 0\end{bmatrix}, \tag{A2}$$

$$A'=\begin{bmatrix}\delta\omega & 0\\ 0 & 0\end{bmatrix}, \tag{A3}$$

$$\tilde{a}(0)=\tilde{a}_0\,, \quad \tilde{b}(0)=1\,. \tag{A4}$$

The form (A1) is equivalent to Eq. (5) and we can now directly apply the results of Sec. II.

(i) Partial ordering (POP). Utilizing Eq. (15) we can write

$$\frac{d}{dt}\begin{bmatrix}\langle a\rangle\\ \langle b\rangle\end{bmatrix} = -iA_0\begin{bmatrix}\langle a\rangle\\ \langle b\rangle\end{bmatrix} - \int_0^t d\tau\,\langle\delta\omega(t)\delta\omega(t-\tau)\rangle\,\bar{\phi}(\tau)\begin{bmatrix}\langle a\rangle\\ \langle b\rangle\end{bmatrix}, \tag{A5}$$

where

$$\bar{\phi}(\tau)=\begin{bmatrix}1 & 0\\ 0 & 0\end{bmatrix}G(\tau)\begin{bmatrix}1 & 0\\ 0 & 0\end{bmatrix}G(-\tau)\,, \tag{A6}$$

$$G(\tau)=e^{-iA_0\tau}\,. \tag{A7}$$

$G(\tau)$ can be evaluated using Green's-function technique (or diagonalization of A_0). The result is

$$\begin{aligned} G_{11}(\tau)&=\frac{E^+e^{-iE^+\tau}-E^-e^{-iE^-\tau}}{E^+-E^-}\,,\\ G_{22}(\tau)&=\frac{(E^+-\Delta)e^{-iE^+\tau}-(E^--\Delta)e^{-iE^-\tau}}{E^+-E^-}\,,\\ G_{12}(\tau)&=\frac{\Omega(e^{-iE^+\tau}-e^{-iE^-\tau})}{E^+-E^-}\,,\\ G_{21}(\tau)&=0\,, \end{aligned} \tag{A8}$$

where

$$E^\pm=\frac{\Delta\pm\alpha}{2}\,, \qquad \alpha=(\Delta^2+4\Omega^2)^{1/2}\,. \tag{A9}$$

Substituting (A8) in (A6) results in

$$\bar{\phi}_{11}(\tau)=\frac{\Delta^2+2\Omega^2(1+\cos\alpha\tau)}{\Delta^2+4\Omega^2}=\frac{\Delta^2+2\Omega^2(1+\cos\alpha\tau)}{\alpha^2}\,,$$
$$\bar{\phi}_{12}(\tau)=\frac{\Omega}{\alpha^2}[\Delta(1-\cos\alpha\tau)+i\alpha\sin\alpha\tau]\,. \quad \text{(A10)}$$

Substitution of (A10) in (A5) results in Eq. (29).

(ii) Chronological ordering (COP). Making use of Eq. (20), we have

$$\frac{d}{dt}\begin{bmatrix}\langle a\rangle\\ \langle b\rangle\end{bmatrix}=-iA_0\begin{bmatrix}\langle a\rangle\\ \langle b\rangle\end{bmatrix}-\int_0^t d\tau\,\langle\delta\omega(t)\delta\omega(\tau)\rangle \times\hat{\phi}(t-\tau)\begin{bmatrix}\langle a(\tau)\rangle\\ \langle b(\tau)\rangle\end{bmatrix}, \quad \text{(A11)}$$

where

$$\hat{\phi}(t-\tau)=\begin{bmatrix}1&0\\0&0\end{bmatrix}G(t-\tau)\begin{bmatrix}1&0\\0&0\end{bmatrix}, \quad \text{(A12)}$$

and G is given by (A8). Substituting (A12) and (A8) in (A11) results in Eq. (32a).

APPENDIX B: DERIVATION OF THE EQUATIONS OF MOTION FOR THE TWO-LEVEL SYSTEM

We start with Eqs. (60a); let us write them in a matrix form

$$\frac{\partial}{\partial t}\vec{\rho}=-iA\cdot\vec{\rho} \quad \text{(B1)}$$

where $\vec{\rho}$ is a vector whose components are ρ_z, $\tilde{\rho}_{ab}$, and $\tilde{\rho}_{ba}$. We first separate A into the fluctuating part (A') and the rest (A_0)

$$A=A_0+A'\,, \quad \text{(B2)}$$

where

$$A'=\begin{bmatrix}0&0&0\\0&\delta\omega(t)&0\\0&0&-\delta\omega(t)\end{bmatrix}. \quad \text{(B3)}$$

For evaluating the reduced equations of motion we define the transformation

$$\begin{bmatrix}|+\rangle\\ |-\rangle\end{bmatrix}=\begin{bmatrix}-\sin\frac{1}{2}\theta&\cos\frac{1}{2}\theta\\ \cos\frac{1}{2}\theta&\sin\frac{1}{2}\theta\end{bmatrix}\begin{bmatrix}|a\rangle\\ |b\rangle\end{bmatrix}\,, \quad \text{(B4)}$$

where

$$\sin\theta=\frac{2\Omega}{\alpha},\quad \cos\theta=\frac{\Delta}{\alpha}\,,$$
$$\alpha=(\Delta^2+4\Omega^2)^{1/2},\quad E^{\pm}=\frac{\Delta\pm\alpha}{2}\,. \quad \text{(B5)}$$

The appropriate transformation in Liouville space is

$$\begin{bmatrix}\rho_{++}-\rho_{--}\\ \tilde{\rho}_{+-}\\ \tilde{\rho}_{-+}\end{bmatrix}=\begin{bmatrix}-\cos\theta&-\sin\theta&-\sin\theta\\ -\frac{1}{2}\sin\theta&-\sin^2\frac{1}{2}\theta&\cos^2\frac{1}{2}\theta\\ -\frac{1}{2}\sin\theta&\cos^2\frac{1}{2}\theta&-\sin^2\frac{1}{2}\theta\end{bmatrix} \times\begin{bmatrix}\rho_{aa}-\rho_{bb}\\ \tilde{\rho}_{ab}\\ \tilde{\rho}_{ba}\end{bmatrix}, \quad \text{(B6)}$$

so that in the new representation we have

$$e^{iA_0\tau}=\begin{bmatrix}1&0&0\\0&\xi&0\\0&0&\xi^*\end{bmatrix},\quad \xi=e^{i\alpha\tau}\,. \quad \text{(B7)}$$

In the POP we have to evaluate the following product of matrices:

$$A'(t)Se^{-iA_0\tau}SA'(t-\tau)Se^{iA_0\tau}S\,,$$

where S is the transformation matrix defined in (B6) and $e^{iA_0\tau}$ is given by (B7). Carrying out this multiplication and substitution in Eq. (15) results in Eq. (61a).

For the COP we have to evaluate the following product:

$$A'(t)S\exp[-iA_0(t-\tau)]SA'(\tau)\,,$$

and substitute in Eq. (20), which results in Eq. (64a).

[1]R. Zwanzig, Physica 30, 1109 (1964).
[2](a) M. Lax, Phys. Rev. 145, 110 (1966); (b) J. Phys. Chem. Solids 25, 487 (1964).
[3]W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).
[4](a) P. N. Argyres and P. L. Kelley, Phys. Rev. 134, A98 (1964); (b) J. H. Freed, J. Chem. Phys. 49, 376 (1968); (c) B. Yoon, J. M. Deutch, and J. H. Freed, *ibid.* 62, 4687 (1975).
[5]For a recent review see A. Ben-Reuven, Adv. Chem. Phys. 33, 235 (1975).
[6]W. H. Miller, Adv. Chem. Phys. 25, 63 (1974).
[7]S. G. Rautian and I. I. Sobel'man, Sov. Phys. Usp. 9, 701 (1967).
[8](a) R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. Ter-Haar (Oliver and Boyd, Edinburgh, 1962); (b) R. Kubo, in *Advances in Chemical Physics*, Vol. 15; edited by K. E. Shuler (Wiley, New York, 1969), (c) A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961).
[9](a) D. Von der Linde, A. Laubereau, and W. Kaiser,

Phys. Rev. Lett. 26, 954 (1971); (b) A. Laubereau, Chem. Phys. Lett. 27, 600 (1974).
[10](a) B. R. Mollow, Phys. Rev. 188, 1969 (1969); Phys. Rev. A 2, 76 (1970); (b) D. L. Huber, Phys. Rev. 158, 843 (1967); 170, 418 (1968); 178, 93 (1969); (c) C. Cohen Tannoudji, in *Frontiers in Laser Spectroscopy*, Les Houches Summer School 1975, edited by R. Balian, S. Haroche, and S. Liberman (North-Holland, Amsterdam, 1975).
[11]For a recent review, see V. S. Letokhov and C. B. Moore, Sov. J. Quantum Electron. 6, 129 (1976).
[12]D. Zvijac, S. Mukamel, and J. Ross, J. Chem. Phys. 67, 2007 (1977).
[13]S. Adelman and J. D. Doll, J. Chem. Phys. 61, 4242 (1974); 62, 2518 (1975).
[14]Y. E. Perlin, Sov. Phys. Usp. 6, 542 (1964).
[15](a) R. Kubo, T. Takagahara, and E. Hanamura, in Proceedings of Oji Seminar on Physics of Highly Excited States in Solids (Springer, Berlin, to be published); (b) T. Takagahara, Ph.D. thesis (University of Tokyo, 1976) (unpublished).
[16]R. Kubo, J. Math. Phys. 4, 174 (1963).
[17]U. Fano, Phys. Rev. 131, 259 (1963).
[18]H. Mori, Prog. Theor. Phys. 33, 423 (1965).
[19](a) S. Mukamel and J. Jortner, J. Chem. Phys. 65, 5204 (1976); (b) N. Bloembergen, C. D. Cantrell, and D. M. Larsen, in *Proceedings of the Nordfjord Conference*, edited by A. Mooradian, T. Taeger, and P. Stokseth (Springer, Berlin, 1976); (c) J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. 38, 1131 (1977); (d) S. Mukamel, in Proceedings of the ICOMP Conference on Multiphoton Processes, Rochester, 1977 (unpublished).
[20]M. Tokuyama and H. Mori, Prog. Theor. Phys. 55, 411 (1976).
[21]R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).
[22]J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. 17, 227 (1945).
[23](a) L. I. Gudzenko and S. I. Yakovlenko, Sov. Phys.-JETP 35, 877 (1972); (b) V. S. Lisista and S. I. Yakovlenko, *ibid.* 39, 759 (1974); (c) R. W. Falcone, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A 15, 1333 (1977).
[24]P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953).
[25]N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).