Relationship between a nonlinear response and relaxation induced by colored noise

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The nonlinear response to external disturbances of a system of interest $\mathcal{A}$ (the "atom") in contact with a thermal bath is studied. The central issue is the relationship between the nonlinear susceptibility and the equilibrium relaxation spectra of observables of $\mathcal{A}$. Paralleling the results of the linear-response theory, the nth-order nonlinear susceptibility is factorized by quantum-mechanical arguments into two terms pertaining to the disturbances and the spin-bath system, respectively. The role of slow atom states, i.e., states relaxing on times T longer than the bath correlation time τ_c, is pointed out, by recurring to recent findings on their general features [Phys. Rev. A **46**, 6222 (1992)]. In the frame of a stochastic picture of the bath and a multilevel scheme of the system $\mathcal{A}$, the conditions under which the nonlinear susceptibility provides the spectrum of the slow atom states are clarified. Illustrations are drawn from magnetic resonance to demonstrate that techniques based on the nonlinear response of a spin system to multiple continuous waves compete favorably with pulsed techniques to provide information on longitudinal spin relaxation.

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I. INTRODUCTION

One of the major achievements of the linear-response theory (LRT) [1,2] is to state that the linear response of a system $\mathcal{C}$ to an external disturbance $F(t)$ is deducible from the relaxation behavior in the absence of the disturbance itself. Let H be the Hamiltonian of the isolated system $\mathcal{C}$. The dynamical motion determined by H is usually referred to as the "natural motion" of the system $\mathcal{C}$. If the perturbation energy V due to the presence of $F(t)$ is represented by

$$V(t)=BF(t) , \tag{1.1}$$

where B is an observable of $\mathcal{C}$ and $F(t)$ is classical, periodic, i.e., $F(t)=F_0\cos(\omega t)$, then the linear response $\Delta A(t)$, defined as the deviation of the observable A from its unperturbed value, will be written as

$$\Delta A(t)=\mathrm{Re}\{\chi(\omega)F_0\exp(i\omega t)\} , \tag{1.2}$$

where $\mathrm{Re}\{Z\}$ means the real part of Z. If the system $\mathcal{C}$ is in canonical equilibrium at temperature $T=1/k_B\beta$, the complex susceptibility $\chi(\omega)$ is given by the general equation ($h/2\pi=1$ and $i^2=-1$)

$$\chi(\omega)=\int_0^\infty \Phi_{BA}(t)\exp(-i\omega t)dt \tag{1.3a}$$

$$=\chi_0+i\omega\beta\int_0^\infty \Psi_{BA}(t)\exp(-i\omega t)dt . \tag{1.3b}$$

$\Phi_{BA}(t)$ is the response function, i.e., the response of $\Delta A(t)$ to the pulsed force $F(t)\approx\delta(t)$, whereas $-\Psi_{BA}(t)$ is the relaxation function accounting for the relaxation of $\Delta A(t)$ after removal of the outer (static) disturbance at $t=0$. From Eq. (1.3) it follows that $\Phi_{BA}(t)$ is the time derivative of $\beta\Psi_{BA}(t)$ and $\chi_0=-\beta\Psi_{BA}(0)$ and

$$\Phi_{BA}(t)=i\,\mathrm{Tr}\{\rho_c[B,A(t)]\} , \tag{1.4}$$

where $[X,Y]=XY-YX$, ρ_c is the equilibrium density matrix of the system $\mathcal{C}$, and

$$\Psi_{BA}(t)=\beta^{-1}\int_0^\beta d\lambda\,\mathrm{Tr}\{\rho_c B(-i\lambda)A(t)\}$$
$$\cong\mathrm{Tr}\{\rho_c B(0)A(t)\} . \tag{1.5}$$

In the second line of Eq. (1.5) high temperature is assumed. If $\Psi_{BA}(\infty)\neq 0$ the limit value must be subtracted from the right-hand side of Eq. (1.5). Equation (1.5) follows by assuming canonical equilibrium [1,2]. In Eq. (1.4) $A(t)$ denotes the natural motion of A, according to

$$\dot{A}(t)=i[H,A] . \tag{1.6}$$

Equations (1.2)–(1.5) relate the linear response to the natural relaxation behavior. If the nonlinear response of the system $\mathcal{C}$ is stimulated by single or multiple external disturbances, Eq. (1.2) is augmented to

$$\Delta A(t)=\mathrm{Re}\left\{\sum_k \chi^{(1)}(\omega_k)F_{0k}\exp(i\omega_k t)\right.$$
$$+\sum_{k_1,k_2}\chi^{(2)}(\omega_{k_1},\omega_{k_2})F_{0k_1}F_{0k_2}$$
$$\left.\times\exp[i(\omega_{\kappa_1}+\omega_{\kappa_2})t]\right\}\cdots . \tag{1.7}$$

Evaluating $\Delta A(t)$ via Eq. (1.7) is meaningful if the amplitudes $F_{01},F_{02},\ldots$ are small enough. Since the system $\mathcal{C}$ will be considered in equilibrium before the disturbances are acted on, this implies that the nonlinear response originates from states weakly out of equilibrium.

The present paper intends to elucidate the relationship existing between $\chi^{(1)},\chi^{(2)},\ldots$ and the response and relaxation functions $\Phi_{BA}(t)$ and $\Psi_{BA}(t)$. In linear condition this relation is assessed by Eq. (1.3). It is a common belief that in nonlinear condition such simple relations are

lost and that nonlinear response is, as a matter of fact, useless to provide insight into the equilibrium relaxation behavior of the system $\mathcal{C}$.

Beyond the theoretical interest, the present investigation is also motivated by the experimental work. Many spectroscopic studies obtain information on Φ_{BA} and Ψ_{BA} by measuring $\chi(\omega)$ in the frequency domain or by preparing the system of interest in some nonequilibrium state whose relaxation is then followed in the time domain ("pump and probe" experiment). Both methodologies present limitations and drawbacks from the standpoint of the interpretation. Furthermore, in some cases, e.g., in magnetic resonance, practical studies put extreme, sometimes unmatched, demands on the experimental and technical conditions beyond the limits of the typical figures for state-of-the-art components [3], so it seems proper to investigate alternative procedures to measure Φ_{BA} and Ψ_{BA}. As a further comment, the choice of investigating the nonlinear response to small-amplitude fields is also motivated by the current trends in the field of magnetic resonance, traditionally the branch of spectroscopy where relaxation effects are a major issue [4].

An analysis of the open literature exposes the lack of a satisfactory investigation of the relationship existing between the nonlinear susceptibilities and the relaxation and response functions. This is somewhat surprising in that Kubo himself in his classic paper [1] touched on this point [see Eqs. (2.25)–(2.29)]. The subject was considered by Miyake and Kubo in the related context of transport theory [5] and, more explicitly, by Tani [6] and Zubarev [7]. In all the papers it is presumed that, at the initial time, the system of interest is in thermal equilibrium and that, after the external disturbances are switched on, it is *isolated* by the thermal bath. This assumption is very crude, since it neglects all the relaxation phenomena induced by the bath. A first attempt by Kalashnikov to circumvent this drawback led to a relation between the response and the disturbance formally equivalent to Eq. (1.2) with a time-dependent susceptibility $\chi(t)$ [8]. Huber and van Vleck discussed the resonant *linear* absorption and evaluated Eq. (1.3) for a two-level system [9]. Huber considered the resonant scattering of photons from an atom-lattice system, namely, a *second-order* process, and derived expressions for the coherent (Rayleigh), incoherent, and fluorescence terms [10,11]. As the analysis is limited to a two-level system, the Raman effect is not recovered. All the above papers are characterized by purely statistical treatment of the problem. A strong impetus was given by the introduction of stochastic approaches which are able to take into explicit consideration the role of the fluctuations [12–14]. Stochastic models depict the environment surrounding the system of interest, i.e., the bath, by introducing a limited set of classical random variables. This approach usually neglects the reaction of the system of interest on the bath itself. The stochastic approaches were applied to the resonant scattering of photons by Huber in a number of papers [15–18]. Second-order optical processes were also extensively investigated by Kubo and co-workers in an extensive series of papers in the framework of stochastic theory [19–25]. The emphasis is on the interaction between the system under observation and its environment. This interaction may occur in the initial or final state of the optical process, but special features result if an intermediate-state interaction takes place. The role played by the fluctuations in determining the Rayleigh (elastic), Raman, and fluorescence (inelastic) components present in the light scattering by multilevel atoms is explained by the authors. Relevant to the present investigation are both the paper by Wodkiewicz and Eberly who discussed the effects of dichotomic random noise on the Bloch equations [26] and the paper by Brown and Ciftan who present a model for a system of N two-level atoms being driven by a monochromatic radiation field [27]. These latter deal with the bath effects not in a systematic way by simply introducing at a certain stage an ansatz, but by applying their equations to many model problems such as superradiance, photon echoes, and bistability. The present author and his collaborators investigated the role of the fluctuations in affecting the line shape by using the generalized Langevin equation [28] and developed a proper generalization of the customary Bloch equation to investigate the basic feature of the nonlinear response of a two-level system acted on by a multiple radiation field [29,30]. In Refs. [29, 30] the emphasis was laid on the atom-radiation interaction, whereas relaxation effects were relegated to the customary relaxation times T_1 and T_2.

In a recent paper [31], hereafter referred to as I, the author and his co-workers have reported on some peculiarities of the relaxation induced by colored noise in multilevel systems. The central issue was to clarify the conditions under which scale separation between the finite correlation time τ_c and the relaxation times takes place. In particular, it was pointed out that the longitudinal relaxation, i.e., the relaxation of populations, is *slow,* namely, $T_1 \gg \tau_c$, provided that the amplitude Δ of the fluctuating fields is smaller than the largest level spacing. This feature will be exploited in the present work to expose the relationship existing between the nonlinear response and the slow relaxation. Following I, the analysis is based on a stochastic model. This is regarded as an advantage since stochastic models can cover a wide category of physical cases from a unified point of view. Furthermore the calculations may be carried out by nonperturbative methods. The model separates the system $\mathcal{C}$ as the system of interest $\mathcal{A}$, to be coupled to the external forces, and the bath $\mathcal{B}$, i.e., the irrelevant degrees of freedom, which is assumed stochastic and colored, i.e., with finite value of τ_c. As in I, the system of interest $\mathcal{A}$ will be either a two-level or a four-level system. A full quantum treatment of both the external disturbances and the system of interest $\mathcal{A}$ is accomplished. Second quantization formalism proved useful by recovering time-independent Hamiltonians. A nonperturbative, systematic treatment of the coupling between the system of interest $\mathcal{A}$ and the irrelevant degrees of freedom collected in $\mathcal{B}$ is introduced in terms of the stochastic Liouville operator (SLO) [2,14] and the generalized Langevin equations (see I for details). The treatment avoids all the delicate questions on convergence to be tackled when using the cumulant expansion

method [32] to which, however, it reduces under time scale separation condition (see I).

The paper is organized as follows. In Sec. II the general framework is outlined on a pure quantum-mechanical basis. The main outcome of the analysis is the factorization of the response at a definite perturbation order as the product of two terms $\mathfrak{R}$ and $\mathfrak{A}$. The former depends only upon the degrees of freedom of the external disturbances, the latter depends only upon the degrees of freedom of the system of interest and the bath. This feature has not been pointed out by previous analysis. On account of it, the approach proves to be a direct extension of the standard LRT. In cases of interest $\mathfrak{R}$ may be reduced to trivial expressions. The term $\mathfrak{A}$ will be expressed as a product of continued fractions, irrespective of the particular Markovian stochastic process considered. In Sec. III a general stochastic picture of the bath will be outlined. In Sec. IV the system of interest will be modeled. In Sec. V applications will be presented. Finally, our conclusions will be summarized.

II. EXACT RESULTS FROM QUANTUM MECHANICS

A. Generalities

Let us consider the situation usually met in spectroscopy (Fig. 1): a system of interest (the "atom") with Hamiltonian H_A is acted on—via a suitable interaction V—by external radiation fields $\mathcal{R}$ with Hamiltonian H_R such that $H_R^{\times}H_A=0$ ($A^{\times}B\equiv AB-BA$). The system $\mathcal{A}$ is in turn embedded in a larger one, which behaves as a thermal bath $\mathcal{B}$ with Hamiltonian H_B. Their mutual interaction is accounted for by a term H_{AB}. With the above definitions some commutation rules follow, namely, $H_R^{\times}H_A=H_R^{\times}H_B=H_B^{\times}H_A=H_R^{\times}H_{AB}=H_B^{\times}V=0$. In particular, it is assumed that negligible coupling exists between radiation and bath states. The total Hamiltonian H_T reads

$$H_T\equiv H_A+H_R+H_B+H_{AB}+V\ . \tag{2.1}$$

The characterization of both the bath $\mathcal{B}$ and the radiation fields $\mathcal{R}$ will be accomplished later on. It is also assumed that the coupling between the radiation and the system $\mathcal{A}$ follows from the interaction between the external fields and the spin S of the system $\mathcal{A}$. We adopt the point of view of Heisenberg and describe the dynamical behavior of the observables of the system $\mathcal{A}$ by resorting to the language of superoperators [2]. In this framework the states of the system $\mathcal{A}$ are indicated by kets $|S,\sigma\rangle\equiv|S\rangle|\sigma\rangle$. $|S\rangle$ is an operator acting in the spin space, whereas $\sigma=\{\sigma_1,\sigma_2,\dots\}$ are further operators which make complete the overall set. To avoid any misunderstanding, the usual kets will be indicated by the notation $|\cdots\rangle\rangle$ throughout the paper. Furthermore, the shorthand notation $|S,I_\sigma\rangle\equiv|S\rangle$, where I_σ is the identity in the subspace spanned by σ, is adopted.

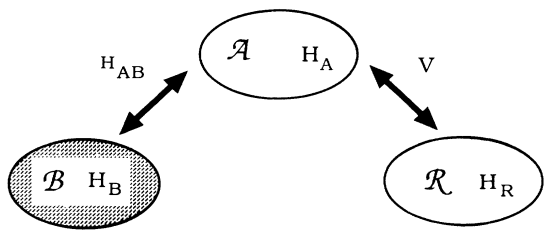

FIG. 1. Schematic view of a spectroscopic experiment.

Let A be the observable of interest of the system $\mathcal{A}$. The first step of the analysis consists in developing a suitable perturbative scheme on V to take advantage of the small amplitudes of the external disturbances. The goal is to express the nonlinear response of the system $\mathcal{A}$ in terms of the unperturbed Hamiltonian H of the system $\mathcal{A}\otimes\mathcal{B}$, namely,

$$H\equiv H_A+H_{AB}+H_B\ . \tag{2.2}$$

Because of Eq. (1.6), the retarded Green function of the complete system is defined as [33]

$$K_T(t,t')\equiv\Theta(t-t')\exp[iH_T^{\times}(t-t')]\ , \tag{2.3}$$

where $\Theta(t)$ is the Heaviside step function [$\Theta(t)=1$ if $t\geq 0$, $\Theta(t)=0$ otherwise] and [2]

$$\exp[iH_T^{\times}t]X\equiv\exp[iH_Tt]X\exp[-iH_Tt]\ . \tag{2.4}$$

Let us consider the retarded Green function $K_T(t,t')$ of the overall system $\mathcal{A}\otimes\mathcal{B}\otimes\mathcal{R}$. It can be shown that [33]

$$K_T(t,t')=K_0(t,t')+i\int_{-\infty}^{+\infty}dt_1K_0(t,t_1)V^{\times}K_T(t_1,t')\ , \tag{2.5}$$

where $K_0(t,t_1)$ is the retarded Green function of the system in the absence of the coupling V, namely,

$$K_0(t,t')=\Theta(t-t')\exp[i(H+H_R)^{\times}(t-t')]\ . \tag{2.6}$$

Starting from the initial time t_0, the time evolution of the observable of interest $A(t)$ is evaluated as

$$A(t)=\mathrm{Tr}_{[\mathcal{A},\mathcal{R},\mathcal{B}]}\{\rho_A\rho_R\rho_BK_T(t,t_0)A\}\ , \tag{2.7}$$

where the trace operation is performed on the degrees of freedom of the systems $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{R}$ weighted by their density matrices ρ_A, ρ_B, and ρ_R, respectively (possible correlations at $t=t_0$ between atom, radiation, and bath are neglected). Since the stationary state of $A(t)$ is of interest, henceforth the time t is understood to be much larger than t_0 to allow the decay of any transient effect subsequent to the switching on of the disturbances. The steady-state signal $\Delta A(t)$ is the variation of the observable with respect to the unperturbed value. By inserting Eq. (2.5) into Eq. (2.7) one obtains for $\Delta A(t)$

$$\Delta A(t)=i\mathrm{Tr}_{[\mathcal{A},\mathcal{R}]}\left\{\rho_A\rho_R\int_{-\infty}^{\infty}dt_1K_R(t,t_1)\times V^{\times}\langle K_T(t_1,t_0)\rangle A\right\} \tag{2.8}$$

since $H^{\times}(\rho_A\rho_B)=0$ and

$$K_R(t,t')\equiv\Theta(t-t')\exp[iH_R^{\times}(t-t')]\ ,\qquad \langle X\rangle\equiv\mathrm{Tr}_{[B]}\{\rho_BX\}\ . \tag{2.9}$$

Equation (2.5) can be iteratively solved to provide a perturbative series in ascending powers of V:

$$K_T(t,t_0)=\sum_{n=0}^{\infty} i^{n-1}\int_{-\infty}^{\infty} dt_1 dt_2 \cdots dt_{n-1} K_0(t,t_{n-1}) \times \cdots V^{\times} K_0(t_2,t_1) \times V^{\times} K_0(t_1,t_0) \ . \tag{2.10}$$

The Laplace transform of $\Delta A(t)$, $\Delta\hat{A}(z)$, is a central quantity in analyzing the harmonic structure of the response

$$\Delta\hat{A}(z)=\int_0^{\infty}\Delta A(t)e^{-zt}dt \ . \tag{2.11}$$

After substituting Eq. (2.10) into Eq. (2.8), $\Delta\hat{A}(z)$ can be expressed as a sum of the contributions $\Delta\hat{A}^{(n)}$ at the different order of perturbation:

$$\Delta\hat{A}(z)=\sum_{n=1}^{\infty}\Delta\hat{A}^{(n)}(z) \ , \tag{2.12}$$

where $\Delta\hat{A}^{(n)}$ is found:

$$\Delta\hat{A}^{(n)}(z)=i^n \mathrm{Tr}_{[\mathcal{A},\mathcal{R}]}[\rho_A\rho_R G_R(z)\langle V^{\times}G_0(z)V^{\times}G_0(z)\cdots V^{\times}G_0(z)A] \ , \tag{2.13}$$

where the averaged term $\langle\ \rangle$ contains n terms. $G_0(z)$ and $G_R(z)$ are the Laplace transforms of $K_0(t,t')$ and $K_R(t,t')$, respectively,

$$G_0(z)\equiv\frac{1}{z-i(H^{\times}+H_R^{\times})}, \quad G_R(z)\equiv\frac{1}{z-iH_R^{\times}} \ . \tag{2.14}$$

To proceed further, an explicit form of the perturbation operator V is needed. This form will be discussed in the next section.

B. Factorization of the response

Let us suppose that $\bar{k}$ different waves are acting on the $\mathcal{A}$ system. The Hamiltonian of the free fields H_R takes the form [33]

$$H_R=\sum_{k=1}^{\bar{k}}\omega_k a_k^{\dagger}a_k=\sum_{k=1}^{\bar{k}}\omega_k a_{-k}a_k \ . \tag{2.15}$$

For the kth mode, $\omega_k=2\pi\nu_k$, ν_k is the frequency, and a_k and $a_{-k}\equiv a_k^{\dagger}$ are the related annihilation and creation operators, respectively.

The application of $G_0(z)$ on a vector of the $\mathcal{A}\otimes\mathcal{B}\otimes\mathcal{R}$ space factorizes according to

$$G_0(z)\left[\prod_k (a_{-k})^{n_k}a_k^{m_k}X\right] = \prod_k (a_{-k})^{n_k}a_k^{m_k}G\left[z+i\sum_k (m_k-n_k)\omega_k\right][X] \ , \tag{2.16}$$

where X is a generic operator of the system $\mathcal{A}\otimes\mathcal{B}$ whose propagator $G(z)$ is given by

$$G(z)\equiv\frac{1}{z-iH^{\times}}=\frac{1}{z-i(H_A^{\times}+H_B^{\times}+H_{AB}^{\times})} \ . \tag{2.17}$$

To analyze the averaged term $\langle V^{\times}G_0(z)V^{\times}G_0(z)\cdots V^{\times}G_0(z)\rangle$ included in Eq. (2.13) the explicit form of the interaction V must be defined. We assume that the radiation field is coupled to the electron spin of the system $\mathcal{A}$. In the long-wavelength approximation for the magnetic field $\mathcal{B}$, V reads as [33]

$$\begin{aligned} V&=-\gamma\mathbf{S}\cdot\mathbf{B} \\ &=\sum_{k=1}^{\bar{k}}\lambda_k\mathbf{S}\cdot(a_k\mathbf{e}_k+a_k^{\dagger}\mathbf{e}_k^{*}) \\ &=\sum_{k=-\bar{k}}^{\bar{k}}\lambda_k S_k a_k \ . \end{aligned} \tag{2.18}$$

$\mathbf{S}$ is the spin operator for magnetic species with magnetogyric factor γ, $\mathbf{e}_k$ is a unit vector describing the polarization state of the kth mode of the field, and $\mathbf{e}_k^{*}$ is its complex conjugate. The notations $\mathbf{e}_{-|k|}\equiv\mathbf{e}_k^{*}$, $S_k\equiv\mathbf{S}\cdot\mathbf{e}_k$, $S_{-|k|}\equiv\mathbf{S}\cdot\mathbf{e}_k^{*}$ are introduced. The strength of the kth mode is $\lambda_{|k|}=\lambda_{-|k|}$ with $\lambda_0=0$. In the case of a cavity with volume $\mathcal{V}$, λ_k is expressed as

$$\lambda_k=\gamma\left[\frac{\omega_k}{2\epsilon_0 c^2\mathcal{V}^3}\right]^{1/2} , \tag{2.19}$$

where ϵ_0 and c are the electric permittivity of free space and the velocity of light, respectively.

The bilinear structure of V and the repeated application of the disentanglement property [Eq. (2.16)] yield for the nth order averaged term $\langle\ \rangle$ of Eq. (2.13)

$$\langle V^{\times}G_0(z)V^{\times}G_0(z)\cdots V^{\times}G_0(z)\rangle A=\sum_{k_1,\ldots,k_n=-\bar{k}}^{\bar{k}}\lambda_{k_1}\cdots\lambda_{k_n}a_{k_n}\cdots a_{k_1}\langle S_{k_n}^{\times}G(z_{k_n})\cdots S_{k_2}^{\times}G(z_{k_2})S_{k_1}^{\times}G(z_{k_1})\rangle A \ . \tag{2.20}$$

The different arguments z_k at which the propagator $G(z_k)$ must be evaluated are derived according to the following iteration scheme:

$$\begin{aligned} &z_{k_1}=z \ , \\ &z_{k_{m+1}}=z_{k_m}+i\,\mathrm{sgn}(k_m)\omega_{k_m} \ , \\ &m\le n-1 \ , \end{aligned} \tag{2.21}$$

where $\mathrm{sgn}(x)$ provides the sign of x.

We are in a position to prove that the response to the applied fields computed at the nth order with respect to V, namely, $\Delta\hat{A}^{(n)}(z)$, can be factorized.

By taking advantage of Eq. (2.20), Eq. (2.13) can be cast in the convenient form

$$\Delta\hat{A}^{(n)}(z)=\sum_{k_1,\ldots,k_n=-\bar{k}}^{\bar{k}}\frac{1}{z+i\sum_{p=1}^{n}\mathrm{sgn}(k_p)\omega_{k_p}}\mathfrak{R}_{\{k_1,\ldots,k_n\}}\mathfrak{A}_{\{k_1,\ldots,k_n\}}(z)\ , \tag{2.22}$$

where

$$\begin{aligned}&\mathfrak{R}_{\{k_1,..,k_n\}}=i^n\lambda_{k_1}\cdots\lambda_{k_n}\mathrm{Tr}_{\{\mathcal{R}\}}[\rho_R a_{k_1}\cdots a_{k_n}\}\ ,\\ &\mathfrak{A}_{\{k_1,\ldots,k_n\}}(z)=\mathrm{Tr}_{\{\mathcal{A}\}}\{\rho_A\langle S_{k_n}^{\times}G(z_{k_n})\cdots S_{k_2}^{\times}G(z_{k_2})S_{k_1}^{\times}G(z_{k_1})\rangle A\}\ .\end{aligned} \tag{2.23}$$

The $\mathfrak{R}$ term *depends only on variables of the applied fields,* whereas the $\mathfrak{A}$ term *depends only on variables of the bath and the system* $\mathcal{A}$. Henceforth, these terms will be referred to as the radiation term and the atom-bath term, respectively.

The poles on the imaginary axis of the right-hand side of Eq. (2.22) yield the discrete frequency spectrum of $\Delta\hat{A}^{(n)}(z)$ in regime condition, as one easily proves by inverting the Laplace transform and resorting to Cauchy's integral formula (the residues of poles with a real part contribute to the transient). By inspection of the analytic properties of $G(z)$, one realizes the imaginary poles are only present in the first term on the right-hand side of Eq. (2.22) [34]. Therefore the spectrum of $\Delta\hat{A}^{(n)}(z)$ exhibits components at frequencies $\bar{\omega}$ such as

$$\bar{\omega}=-\sum_{p=1}^{n}\mathrm{sgn}(k_p)\omega_{k_p}\ , \tag{2.24}$$

with amplitudes given by the residue $R_n(\bar{\omega})$:

$$R_n(\bar{\omega})\equiv\sum_{k_1,..,k_n=-\bar{k}}^{\bar{k}\,\prime}\mathfrak{R}_{\{k_1,\ldots,k_n\}}\mathfrak{A}_{\{k_1,\ldots,k_n\}}(i\bar{\omega})\ . \tag{2.25}$$

The prime signals that the sum must be restricted to the terms allowed by possible selection rules. These latter ones pick out the correct sequences $S_{k_1}^{\times},S_{k_2}^{\times},\ldots,S_{k_n}^{\times}$ appearing in the $\mathfrak{A}$ term. Equation (2.24) instructs us about how to evaluate the frequency spectrum of the nonlinear response at nth order. For an allowed n-photon process (identified by the string $k_1,k_2,\ldots,k_n$), if the pth step involves the emission (absorption) of a photon of frequency ω_{k_p}, this event will contribute with a term $+\omega_{k_p}$ $(-\omega_{k_p})$ to the frequency $\bar{\omega}$ related to the process. The amplitude of the harmonic at the frequency $\bar{\omega}$ is given by Eq. (2.25).

To conclude this section, we summarize the main results obtained by the quantum framework.

(i) Tracing both the amplitude and the frequency of the components of the spectrum of the observable back to the underlying multiphoton process. This feature is not easily recognizable in other treatments, since the evaluation of the amplitude is usually the major problem [35,36].

(ii) Factorizing the response at nth order in two terms $\mathfrak{R}$ and $\mathfrak{A}$. The former pertains to the radiation fields, the latter to the subsystem constituted by the thermal bath and the atom. The factorization rests on the disentanglement property expressed by Eq. (2.16) and motivates the statement that the present approach extends the LRT to the case of nonlinear response of the atom.

In the next paragraphs both the terms $\mathfrak{R}$ and $\mathfrak{A}$ will be discussed thoroughly.

C. Reduction of the radiation term

In an experiment the fields can often be considered as quasiclassical, coherent states $|\omega_k\rangle$ [11,33,35]. The coherent states of the kth oscillator are the eigenstates of the annihilation operator a_k with eigenvalue α_k:

$$a_k|\omega_k\rangle=\alpha_k|\omega_k\rangle,\quad \langle\omega_k|a_k^{\dagger}=\alpha_k^{*}\langle\omega_k|\ . \tag{2.26}$$

The density matrix of the radiation ρ_R becomes

$$\rho_R=|\omega_1\rangle\langle\omega_1|\otimes|\omega_2\rangle\langle\omega_2|\otimes\cdots\otimes|\omega_{\bar{k}}\rangle\langle\omega_{\bar{k}}|\ . \tag{2.27}$$

Let the classical field $\mathbf{B}(t)$ be expressed as

$$\mathbf{B}(t)=\sum_{k=1}^{\bar{k}}B_k[\mathbf{e}_k\exp(-i\omega_k t)+\mathbf{e}_k^{*}\exp(i\omega_k t)]\ , \tag{2.28}$$

where $\mathbf{e}_k$ is the polarization unit vector and $\mathbf{e}_k^{*}$ is its complex conjugate. If the matrix element $\langle\omega_k|V|\omega_k\rangle$ is computed, according to Eq. (2.18), one proves that the eigenvalue α_k of the kth coherent mode $|\omega_k\rangle$, the strength λ_k of its interaction with the spin system, and the classical amplitude B_k fit in the correspondence relation

$$B_k=\frac{\lambda_k|\alpha_k|}{\gamma}\ . \tag{2.29}$$

On quasiclassical states, the radiation term reduces to a simple expression. By inserting Eq. (2.27) into Eq. (2.23),

$$\begin{aligned}\mathfrak{R}_{\{k_1,\ldots,k_n\}}&=i^n\lambda_{k_1}\cdots\lambda_{k_n}\mathrm{Tr}_{\{\mathcal{R}\}}\{\rho_R a_{k_1}\cdots a_{k_n}\}\\ &=i^n\lambda_{k_1}\cdots\lambda_{k_n}\mathcal{N}\{\alpha_{k_1}\cdots\alpha_{k_n}\}\ .\end{aligned} \tag{2.30}$$

The function $\mathcal{N}\{\alpha_{k_1}\cdots\alpha_{k_n}\}$ must be calculated by putting the product $a_{k_1}\cdots a_{k_n}$ in normal order and then replacing a_{k_p} by α_{k_p} $(\alpha_{-|k|}\equiv\alpha_{|k|}^{*})$. In most practical cases the value of $|\alpha_k|$ is so high that normal ordering can be neglected, so yielding the very simple result

$$\Re_{\{k_1,\ldots,k_n\}}=i^n\lambda_{k_1}\cdots\lambda_{k_n}\mathcal{N}\{\alpha_{k_1}\cdots\alpha_{k_n}\}$$
$$\cong i^n\lambda_{k_1}\cdots\lambda_{k_n}\alpha_{k_1}\cdots\alpha_{k_n}$$
$$=(i\gamma)^n\prod_{i=1}^{n}B_{k_i}\ . \tag{2.31}$$

It must be pointed out that the radiation term does not contain information concerning the polarizations of the radiation fields. The polarization states $\mathbf{e}_k$ have been included in the definition of the vertices S_k of the radiation term [Eqs. (2.18), (2.23)] and contribute to "build up" the spectroscopy selection rules.

Equations (2.25) and (2.31) allow the derivation of the explicit expression of the nonlinear susceptibilities $\chi^{(1)},\chi^{(2)},\ldots,\chi^{(n)}$ coming out in the expansion [Eq. (1.7)]

$$\chi^{(n)}[-\operatorname{sgn}(k_1)\omega_{k_1},\ldots,-\operatorname{sgn}(k_n)\omega_{k_n}]$$
$$=(i\gamma)^n\mathfrak{A}_{\{k_1,\ldots,k_n\}}(i\bar{\omega})\ . \tag{2.32}$$

Equation (2.32) pertains to the component at frequency $\bar{\omega}$ [Eq. (2.24)] of the nth-order response. Equation (2.32) evidences the contribution to the frequency $\bar{\omega}$ coming from each step of the n-atom–radiation interactions.

III. STOCHASTIC MODEL OF THE ATOM-BATH INTERACTION

A. Generalities

Until now all the results have been derived in a pure quantum-mechanical way. The factorization of the response expressed by Eq. (2.22) enables us to concentrate only on the unperturbed system $\mathcal{A}\otimes\mathcal{B}$. Nonetheless, in order to reduce the huge number of bath variables to a manageable, reduced set, assumptions must be introduced. In this spirit the bath variables will be replaced with classical stochastic variables, by defining a multicomponent vector $\mathbf{W}=(W_1,W_2,\ldots,W_n)$. It is assumed that the stochastic properties of $\mathbf{W}$ can be described by a Markov, stationary process [37]. The transition probability $p(\mathbf{W},t|\mathbf{W}_0,t_0)\equiv T_\tau(\mathbf{W}|\mathbf{W}_0)$ where $\tau=t-t_0$ fits in the master equation:

$$\frac{\partial}{\partial t}T_\tau(\mathbf{W}|\mathbf{W}_0)=\Gamma_{\mathbf{w}}T_\tau(\mathbf{W}|\mathbf{W}_0)\ . \tag{3.1}$$

The explicit expression of the operator $\Gamma_{\mathbf{w}}$ is

$$\Gamma_{\mathbf{w}}=\int d\mathbf{W}'P(\mathbf{W}|\mathbf{W}')-\left[\int d\mathbf{W}'P(\mathbf{W}'|\mathbf{W})\right]\ . \tag{3.2}$$

$P(\mathbf{W}|\mathbf{W}')$ is the transition probability per unit time from $\mathbf{W}'$ to $\mathbf{W}$. If the range of $\mathbf{W}$ is discrete, the integrals are replaced by sums. Equation (3.1) can be cast in the more intuitive form

$$\frac{\partial}{\partial t}T_\tau(\mathbf{W}|\mathbf{W}_0)=\int d\mathbf{W}'P(\mathbf{W}|\mathbf{W}')T_\tau(\mathbf{W}'|\mathbf{W}_0)$$
$$-\left[\int d\mathbf{W}'P(\mathbf{W}'|\mathbf{W})\right]T_\tau(\mathbf{W}|\mathbf{W}_0)\ . \tag{3.3}$$

By assuming the bath $\mathcal{B}$ to be a closed, finite, isolated system, detailed balance follows [37]:

$$P(\mathbf{W}|\mathbf{W}')T_\infty(\mathbf{W}'|\mathbf{W}_0)=P(\mathbf{W}'|\mathbf{W})T_\infty(\mathbf{W}|\mathbf{W}_0)\ , \tag{3.4}$$

where $T_\infty(\mathbf{W}|\mathbf{W}_0)$ denotes the equilibrium distribution of the stochastic variable $\mathbf{W}$, i.e., $T_\tau(\mathbf{W}|\mathbf{W}_0)$ for $\tau\to\infty$. The detailed-balance property can be applied to the present case, by considering the atom system as a small subsystem of the larger system including the bath. Owing to detailed balance, the general solution of Eq. (3.1) can be conveniently expressed in terms of a proper set of eigenfunctions. To ensure a symmetric form to $\Gamma_{\mathbf{w}}$ let us define a scalar product between any two functions $b(\mathbf{W})$ and $c(\mathbf{W})$ as

$$(b|c)\equiv\int\frac{b^*(\mathbf{W})c(\mathbf{W})}{T_\infty(\mathbf{W}|\mathbf{W}_0)}d\mathbf{W}\ . \tag{3.5}$$

In the above equation a quantumlike notation in terms of round bra and kets has been introduced for the bath states. With respect to the above scalar product $\Gamma_{\mathbf{w}}$ is a symmetric operator, namely, $(b|\Gamma_{\mathbf{w}}c)=(c|\Gamma_{\mathbf{w}}b)=(\Gamma_{\mathbf{w}}b|c)$. Thereby, a complete set of orthornormal eigenvectors is found so that $\Gamma_w b_\lambda=\lambda b_\lambda$, with $\lambda\le 0$. In particular, there is one eigenvalue $\lambda=0$ which is not degenerate with eigenfunction $b_0=T_\infty(\mathbf{W}|\mathbf{W}_0)$. The eigenvalues can be discrete or continuous or both. Henceforth, the notation for discrete eigenvalues denoted by the index λ is used.

The completeness is expressed by

$$\sum_\lambda\frac{b_\lambda^*(\mathbf{W})b_\lambda(\mathbf{W}')}{b_0(\mathbf{W}')}=\delta(\mathbf{W}-\mathbf{W}') \tag{3.6}$$

so that the solution of the master equation with initial $T_0(\mathbf{W}|\mathbf{W}_0)=\delta(\mathbf{W}-\mathbf{W}_0)$ is

$$T_\tau(\mathbf{W}|\mathbf{W}_0)=\sum_\lambda\frac{b_\lambda(\mathbf{W})b_\lambda(\mathbf{W}_0)}{b_0(\mathbf{W}_0)}e^{-\lambda t}\ . \tag{3.7}$$

Equation (3.7) proves that detailed balance is sufficient to ensure symmetrization of $\Gamma_{\mathbf{w}}$ and then an expansion of $T_\tau(\mathbf{W}|\mathbf{W}_0)$ in terms of a basis of eigenvectors.

If the constraint of detailed balance is relaxed, one usually tries to expand $T_\tau(\mathbf{W}|\mathbf{W}_0)$ on a biorthogonal set, which is complete if all the eigenvalues of $\Gamma_{\mathbf{W}}$ are different. In this case the non-Hermitian operator $\Gamma_{\mathbf{W}}$ can always be diagonalized by a similarity transformation. If some eigenvalues coincide, completeness becomes questionable and the procedure is reliable if only a few eigenvalues close to $\lambda=0$ are relevant. Tricks can be applied to special cases. A thorough discussion concerning the case of $\Gamma_{\mathbf{W}}$ coinciding with the Fokker-Planck operator is given by Risken [38].

In a stochastic description the term H_{AB} of the unperturbed Hamiltonian H [Eq. (2.2)], accounting for the interaction between the system $\mathcal{A}$ and the bath $\mathcal{B}$, becomes a function of both the quantum variables of the system $\mathcal{A}$ and the classical stochastic variable $\mathbf{W}$ [$H_{AB}=H_{AB}(\mathbf{W})$]. The feedback of the system $\mathcal{A}$ on the bath is neglected, so that $\Gamma_{\mathbf{W}}$ is independent of the degrees of freedom of the system $\mathcal{A}$. Finally, the quantal Green function $K_T(t)$ [Eq. (2.3)] is replaced by the stochastic propagator $K_T^{(\mathrm{st})}(t)$ [2,37]:

$$K_T^{(\mathrm{st})}(t)=\Theta(t)\exp[\Gamma_T t]\ , \tag{3.8}$$

where Γ_T is the stochastic Liouville operator:

$$\Gamma_T=i[H_A+H_R+H_{AB}(\mathbf{W})+V]^{\times}+\Gamma_{\mathbf{W}}\ . \tag{3.9}$$

Γ_T consists of a conservative part sharing the rigorous character of a Liouville operator built up according to the rules of analytical mechanics and a dissipative one.

In the stochastic scheme the trace operation on the bath variables is replaced by an average on the range of $\mathbf{W}$ weighted by the *classical* equilibrium distribution $\rho_B(\mathbf{W})$:

$$\begin{aligned}&\langle X\rangle \Longrightarrow \langle X\rangle^{(\mathrm{st})}\ ,\\ &\langle X\rangle^{(\mathrm{st})}\equiv\int d\mathbf{W}\,\rho_B(\mathbf{W})X(\mathbf{W})=(b_0|X|b_0)\ .\end{aligned} \tag{3.10}$$

Stochastic assumptions do not affect the general factorization of the response $\Delta A(z)$ [Eq. (2.23)]. The atom-bath term is changed as

$$\mathfrak{A}^{(\mathrm{st})}_{\{k_1,\ldots,k_n\}}(z)=\mathrm{Tr}_{\{\mathcal{A}\}}\{\rho_A\langle S^{\times}_{k_n}G^{(\mathrm{st})}(z_{k_n})\cdots S^{\times}_{k_2}G^{(\mathrm{st})}(z_{k_2})S^{\times}_{k_1}G^{(\mathrm{st})}(z_{k_1})\rangle^{(\mathrm{st})}A\}\ , \tag{3.11}$$

where the deterministic propagator $G(z)$ [Eq. (2.17)] is replaced by the stochastic propagator $G^{(\mathrm{st})}(z)$ defined as

$$G^{(\mathrm{st})}(z)\equiv\frac{1}{z-\Gamma},\quad \Gamma\equiv i[H_A^{\times}+H_{AB}^{\times}(\mathbf{W})]+\Gamma_{\mathbf{W}}\ . \tag{3.12}$$

In conclusion, due to Eqs. (2.22), (2.25), (2.31), and (3.11), in a stochastic framework the nth-order response exhibits a spectrum whose amplitude at frequency $\bar{\omega}$ [Eq. (2.24)] is

$$R_n^{(\mathrm{st})}(\bar{\omega})\equiv(i\gamma)^n\sum_{k_1,\ldots,k_n=-\bar{k}}^{\bar{k}\,\prime}\prod_{i=1}^{n}B_{k_i}\mathfrak{A}^{(\mathrm{st})}_{\{k_1,\ldots,k_n\}}(i\bar{\omega})\ . \tag{3.13}$$

The susceptibility $\chi^{(n)}$ maintains the same form of Eq. (2.32). Henceforth, the superscript "(st)" will be dropped to simplify the notation.

B. Expansion of the atom-bath term

The expression of the atom-bath term $\mathfrak{A}_{\{k_1,\ldots,k_n\}}(z)$ given by Eq. (3.11) is worth noting. It emerges that the central quantity is the propagator $G(z)$ governing the free relaxation of the system $\mathcal{A}$ under the influence exerted by the bath $\mathcal{B}$. In the linear case ($n=1$) the evaluation of the response involves a single matrix element of $G(z)$. Differently, the nonlinear response ($n>1$) is expressed by products of different matrix elements of $G(z)$. By properly designing the experiment, it is possible to select particular matrix elements. This feature discloses a wide-ranging field of applications of the nonlinear spectroscopies and will be brought into sharp focus later.

Let us expand the atom-bath term, as expressed by Eq. (3.11), by inserting identity operators. The reduction of the expression to a manageable form is obtained by observing that the vertices, namely, the superoperators $S^{\times}_{k_r}$, can be expanded on a small set of orthornormal eigenvectors in the case of practical interest $S=\frac{1}{2}$.

Let us define the scalar product between two operators acting in the $\mathcal{A}$ space as

$$\langle X|Y\rangle\equiv\mathrm{Tr}_{\{\mathcal{A}\}}\{X^{\dagger}Y\}\ , \tag{3.14}$$

where $\mathrm{Tr}_{\{\mathcal{A}\}}$ is a trace operation in the $\mathcal{A}$ space and $X^{\dagger}$ the Hermitian conjugate of X [in the $\mathcal{B}$ space the scalar product is defined by Eq. (3.5)]. Indicating x as the direction of $\mathbf{e}_{k_r}$, $S^{\pm}_{k_r}\equiv S_y\pm iS_z$ are eigenoperators of $S^{\times}_{k_r}$ with eigenvalue ±1 and both the identity and S_x are eigenoperators with zero eigenvalue. Therefore for the case $S=\frac{1}{2}$

$$\begin{aligned}\mathbf{S}^{\times}\cdot\mathbf{e}_{k_r}&=\sum_{\sigma_r}|S^{+}_{k_r},\sigma_r\rangle\langle\sigma_r,S^{+}_{k_r}|-|S^{-}_{k_r},\sigma_r\rangle\langle\sigma_r,S^{-}_{k_r}|\\ &=\sum_{\sigma_r=\pm1}\sum_{\sigma_r}\alpha_r|S^{\alpha_r}_{k_r},\sigma_r\rangle\langle\sigma_r,S^{\alpha_r}_{k_r}|\ ,\end{aligned} \tag{3.15}$$

where σ_r denotes further quantum variables rendering the description of the system $\mathcal{A}$ complete. Inserting Eqs. (3.6) and (3.15) in Eq. (3.11) leads to the expansion of the atom-bath term. The matrix element related to the rth propagation assumes the form

$$\begin{aligned}&G^{\alpha_{r+1}k_{r+1}\sigma_{r+1};\alpha_r k_r\sigma_r}_{i_{r+1},i_r}(z)\\ &\quad=(b_{i_{r+1}}|\langle\sigma_{r+1}S^{\alpha_{r+1}}_{k_{r+1}}|G(z)|S^{\sigma_r}_{k_r}\sigma_r\rangle|b_{i_r})\ ,\end{aligned} \tag{3.16}$$

where the upper indices refer to the states of the system $\mathcal{A}$ and the lower ones to the bath states. Now we are in a position to express the atom-bath term [Eq. (3.11)] as

$$\mathfrak{A}_{\{k_1,\ldots,k_n\}}(z)=\sum_{\alpha_1,\ldots,\alpha_n=\pm1}\sum_{i_1,\ldots,i_{n-1}}\sum_{\sigma_1,\ldots,\sigma_n}\langle\rho_A|S^{\alpha_n}_{k_n}\sigma_n\rangle\prod_{r=0}^{n-1}[\alpha_{r+1}G^{\alpha_{r+1}k_{r+1}\sigma_{r+1};\alpha_r k_r\sigma_r}_{i_{r+1},i_r}(z_{k_{r+1}})]\ . \tag{3.17}$$

The indexes i_0 and i_n are limited to $i_0=i_n=0$. $|S^{\alpha_0}_{k_0}\sigma_0\rangle\equiv|A\rangle$. The arguments of $G(z)$ are to be evaluated according to the iteration Eq. (2.21) with $z_{k_1}=z$. Owing to Eq. (2.32), the atom-bath term and the susceptibility may be related by letting $z=i\bar{\omega}$ in Eq. (3.17). For readers' convenience and for later use the explicit expressions of the atom-bath term at frequency $\bar{\omega}$ is derived for $n=1,2,3$:

$$\mathfrak{A}_{\{k_1\}}(i\bar{\omega})=\sum_{\alpha_1=\pm1}\sum_{\sigma_1}\alpha_1\langle\rho_A|S_{k_1}^{\alpha_1}\sigma_1\rangle\langle\sigma_1,S_{k_1}^{\alpha_1}|\langle G(i\bar{\omega})\rangle|A\rangle$$
$$=-i\hat{\Phi}_{S_{k_1};A}(i\bar{\omega})\ . \tag{3.18a}$$

The susceptibility $\chi^{(1)}$ obtained by inserting Eq. (3.18a) in Eq. (2.32) coincides with Eq. (1.3a) ($\rho_C=\rho_A\rho_B$). At higher orders

$$\mathfrak{A}_{\{k_1,k_2\}}(i\bar{\omega})=\sum_{\alpha_1,\alpha_2=\pm1}\sum_{i_1}\sum_{\sigma_1,\sigma_2}\alpha_1\alpha_2\langle\rho_A|S_{k_2}^{\alpha_2}\sigma_2\rangle\langle\sigma_2,S_{k_2}^{\alpha_2}|(b_0|G(i\bar{\omega}+i\,\mathrm{sgn}(k_2)\omega_{k_2})|b_{i_1})|S_{k_1}^{\alpha_1},\sigma_1\rangle$$
$$\times\langle\sigma_1,S_{k_1}^{\alpha_1}|(b_{i_1}|G(i\bar{\omega})|b_0)|A\rangle\ , \tag{3.18b}$$

$$\mathfrak{A}_{\{k_1,k_2,k_3\}}(i\bar{\omega})=\sum_{\alpha_1,\alpha_2,\alpha_3=\pm1}\sum_{i_1,i_2}\sum_{\sigma_1,\sigma_2,\sigma_3}\alpha_1\alpha_2\alpha_3\langle\rho_A|S_{k_3}^{\alpha_3}\sigma_3\rangle$$
$$\times\langle\sigma_3,S_{k_3}^{\alpha_3}|(b_0|G[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]|b_{i_2})|S_{k_2}^{\alpha_2},\sigma_2\rangle$$
$$\times\langle\sigma_2,S_{k_2}^{\alpha_2}|(b_{i_2}|G[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}]|b_{i_1})|S_{k_1}^{\alpha_1},\sigma_1\rangle\langle\sigma_1,S_{k_1}^{\alpha_1}|(b_{i_1}|G(i\bar{\omega})|b_0)|A\rangle\ . \tag{3.18c}$$

Apart from the case $n=1$, in the above expressions it is impossible to identify terms to be interpreted as *equilibrium* correlation functions, since the bath average in the atom-bath term is performed on the overall propagation [see Eq. (3.11)]. This can be understood since the atom and the bath dynamics occur in general on comparable time scales during the propagations governed by G. In Eqs. (3.17) this is signaled by the presence of the matrix elements $(b_i|G(z)|b_j)$ [see Eqs. (3.16)] measuring the degree of correlation between the bath states during the development of the atom state. This correlation vanishes for time intervals of more than τ_c ($\tau_c\approx\lambda_1$ the first eigenvalue of Γ_w in our stochastic picture). The overall average appearing in Eq. (3.11) can be split in a product of averages if the bath correlations vanish during the relaxation of the atom state. The condition is $T\gg\tau_c$, where T is the time scale of the relaxation of the atom state. Atom states relaxing on time scales exceeding τ_c will be referred to as *slow* states.

The splitting process of the overall average can occur in two basic ways.

(i) The observable A itself is slow. In this case the atom-bath term reduces to

$$\mathfrak{A}^{(\mathrm{st})}_{\{k_1,\ldots,k_n\}}(z)=\mathrm{Tr}_{\{\mathcal{A}\}}\{\rho_A\langle S_{k_n}^{\times}G(z_{k_n})\cdots S_{k_2}^{\times}G(z_{k_2})S_{k_1}^{\times}\rangle\langle G(z_{k_1})\rangle A\}\ . \tag{3.19}$$

(ii) The absorption or emission processes set the spin state so that the overall atom state is slow during the following propagation. For example, if the setting occurs at the first atom-radiation interaction, the atom-bath term becomes

$$\mathfrak{A}_{\{k_1,\ldots,k_n\}}(z)=\mathrm{Tr}_{\{\mathcal{A}\}}\{\rho_A\langle S_{k_n}^{\times}G(z_{k_n})\cdots S_{k_2}^{\times}\rangle$$
$$\times\langle G(z_{k_2})\rangle\langle S_{k_1}^{\times}G(z_{k_1})\rangle A\}\ . \tag{3.20}$$

The above cases are general paradigms. The bath state can be assumed to be the equilibrium state Φ_0 in the two vertices 1 and 2 before and after the slow propagation driven by $\langle G(z)\rangle$, respectively. The general treatment of the propagator $\langle G(z)\rangle$ when the atom is in a slow state is discussed in I in terms of proper coarse graining of the time scale. This procedure is correct provided that the new time scale Δt is chosen according to the prescription $T\gg\Delta t\gg\tau_c$.

The case (ii) discussed above is sketched in the Feynman diagram of Fig. 2 [the case (i) is analogous]. The empty dots are the initial states. Waves denote photon absorption or emission occurring in the vertex (black dots). Figure 2(a) depicts the general case of comparable dynamics of the atom and bath states. Figure 2(b) illustrates the coarse-grained view of the relaxation of the slow atom state set by the radiation field at the first vertex. On the scale Δt the only significant amplitudes come from matrix elements involving as right and left bath kets $|b_0)$. On a more physical basis this means that the bath

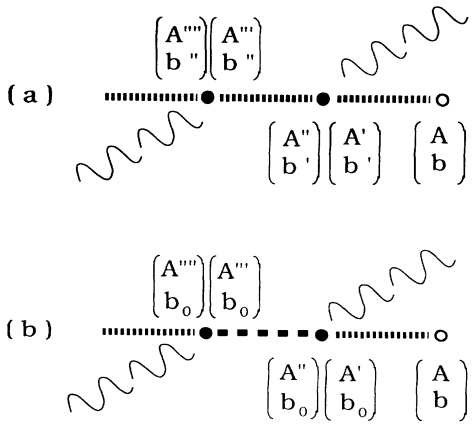

FIG. 2. (a) Normal propagation of the observable A in the presence of two interactions with the external fields. (b) Slow atom state set by the radiation at the first atom-radiation interaction act.

fluctuations can always be thought of as relaxed on the scale Δt.

C. Analytical treatment of the propagator $G(z)$

The amplitudes [Eq. (3.16)] are the central quantities needed to evaluate the atom-bath term included in Eq. (3.17). In this section analytical methods will be outlined to evaluate these amplitudes. The procedures will account for both comparable and separated time scales. The general expression of the amplitudes is

$$\langle B|(b_i|G(z)|b_f)|A\rangle , \tag{3.21}$$

where B and A are atom states and b is a bath state. If atom states are slow, the relevant amplitudes follow from the Laplace transform of

$$\psi_{BA}(t)=(b_0|\langle B|A(t)\rangle|b_0)=\mathrm{Tr}_{\{\mathcal{A}\}}\{B^{\dagger}\langle A(t)\rangle\} . \tag{3.22}$$

$\psi_{BA}(t)$ can be interpreted as a cross correlation function. There is a substantial difference between $\Psi_{BA}(t)$ [Eq. (1.5)] and $\psi_{BA}(t)$. $\Psi_{BA}(t)$ is weighted by the equilibrium density matrix of the atom-bath joint system ρ_C, whereas $\psi_{BA}(t)$ is weighted only by the bath equilibrium distribution. This may be understood since the atom states, during the multiple interactions with the external fields, do not relax to the equilibrium state. Instead, bath fluctuations relax during the time evolution of the slow atom state.

Analytical expressions of the Laplace transform of Eqs. (3.21) and (3.22) can be achieved by resorting to the frame of generalized Langevin equations [28]. On the other hand, Eq. (3.22) can be recast to evidence the average $\langle A(t)\rangle$. The equation of motion of $\langle A(t)\rangle$ is provided by the cumulant expansion [39–41]. The generalized Langevin equation is a more general tool than the cumulant expansion, which is convergent only when good separation between macroscopic and microscopic time scales takes place. Nonetheless, in this case the cumulant expansion delivers a systematic procedure for the elimination of fast variables. Details about the two methodologies are found in the appendixes of I. Below, the main results are summarized.

1. Generalized Langevin equation

Let us consider the quantity $\Psi_{BA}(t)$ defined as

$$\Psi_{BA}(t)=(B,A(t)) , \tag{3.23}$$

where (B,C) denotes a suitable scalar product [Eq. (1.5) shows the usual case of a weighted trace operation]. The time evolution is governed by

$$\dot{A}(t)=iH^{\times}A(t) . \tag{3.24}$$

H is not necessarily a Hermitian operator. The approach based on the generalized Langevin equation expresses the Laplace transform $\hat{\Psi}_{BA}(z)$ of the correlation function $\Psi_{BA}(t)$ as a continued fraction

$$\hat{\Psi}_{BA}(z)=\cfrac{(B,A)}{z-a_0-\cfrac{b_1^2}{z-a_1-\cfrac{b_2^2}{z-a_2-\cdots}}} , \quad (B,A)\neq 0 . \tag{3.25}$$

If the correlations vanish at the initial time, i.e., $(B,A)=0$, one finds the modified expansion

$$\hat{\Psi}_{BA}(z)=i^n\cfrac{(B,H^{\times n}A)z^{-n}}{z-a_0'-\cfrac{b_1'^2}{z-a_1'-\cfrac{b_2'^2}{z-a_2'-\cdots}}} ,$$

$$(B,H^{\times m}A)=0, \quad 0\leq m<n , \tag{3.26}$$

where n is the first integer for which $(B,H^{\times m}A)$ does not vanish. a,a',b,b' are complex numbers.

Analytical expansion of the Laplace transform of $\Psi_{BA}(t)$ is provided by introducing a proper biorthogonal basis set. The set is generated by starting with two seed states $f_0=A$ and $\tilde{f}_0=B$ and iterating for the right states according to

$$\begin{aligned} f_1&=iH^{\times}f_0-a_0f_0 , \\ f_{n+1}&=iH^{\times}f_n-a_nf_n-b_n^2f_{n-1} \end{aligned} \tag{3.27a}$$

and for the left states according to

$$\begin{aligned} \tilde{f}_1&=\tilde{f}_0iH^{\times}-a_0\tilde{f}_0 , \\ \tilde{f}_{n+1}&=\tilde{f}_niH^{\times}-a_n\tilde{f}_n-b_n^2\tilde{f}_{n-1} , \end{aligned} \tag{3.27b}$$

where

$$a_n=\frac{(\tilde{f}_n,iH^{\times}f_n)}{(\tilde{f}_n,f_n)}, \quad b_n^2=\frac{(\tilde{f}_n,f_n)}{(\tilde{f}_{n-1},f_{n-1})} . \tag{3.28}$$

2. Cumulant expansion method

Let us decompose the operator H as

$$H=H_0+H_1 , \tag{3.29}$$

with $H_0=\langle H\rangle$ and $H_1=H-H_0$, according to Eq. (3.10). To deprive the dynamics of $A(t)$ of the "free" motion due to H_0, one defines the interaction representation

$$\begin{aligned} A^{(0)}(t)&=\exp(-iH_0^{\times}t)A(t) , \\ H_1^{(0)\times}(t)&=\exp(-iH_0^{\times}t)H_1^{\times}\exp(iH_0^{\times}t) \end{aligned} \tag{3.30}$$

so that Eq. (3.24) becomes

$$\dot{A}^{(0)}(t)=iH_1^{(0)\times}(t)A^{(0)}(t) . \tag{3.31}$$

Starting from Eq. (3.31) an *exact* equation of motion for the average value of $A^{(0)}(t)$ follows which takes the form

$$\frac{\partial}{\partial t}\langle A^{(0)}(t)\rangle=\mathcal{K}^{(0)}(t)\langle A^{(0)}(t)\rangle , \tag{3.32}$$

with

$$\mathcal{K}^{(0)}(t)=\sum_{m=2}^{\infty}\mathcal{K}_m^{(0)}(t)\ . \tag{3.33}$$

The detailed derivation of Eq. (3.32) can be found in I. The terms $K_m^{(0)}(t)$ are usually named *ordered cumulants* and rules have been derived for building them up [39–41].

For Eq. (3.32) to become of practical interest, we must distinguish between two time scales. The first is the time scale on which $\langle A^{(0)}(t)\rangle$ varies appreciably. We characterize this scale by T_A. The second time scale is determined by the autocorrelation time τ_c of $H_1^{(0)\times}(t)$. As soon as $\tau_c \ll T_A$, the properties of ordered cumulants lead to successive Markovian approximated forms of Eq. (3.32) of a higher and higher order with respect to $H_1^{(0)\times}(t)$, which are effective on the coarse-grained time scale Δt such as $\tau_c \ll \Delta t \ll T_A$. On this scale $\mathcal{K}^{(0)}(t)$ can be replaced by $\mathcal{K}^{(0)}(\infty)$.

At second order Eq. (3.32) reduces to

$$\frac{\partial}{\partial t}\langle A^{(0)}(t)\rangle=\mathcal{K}_2^{(0)}(\infty)\langle A^{(0)}(t)\rangle\ , \tag{3.34}$$

with

$$\mathcal{K}_2^{(0)}(\infty)=\int_0^{\infty}d\tau_1 k_2^{(0)}(t|t-\tau_1)\ , \tag{3.35}$$

where

$$k_2^{(0)}(t|t-\tau)=-\langle H_1^{(0)\times}(t)H_1^{(0)\times}(t-\tau)\rangle\ . \tag{3.36}$$

The second-order cumulant $\mathcal{K}_2^{(0)}(\infty)$ can be separated in a Hermitian and anti-Hermitian part, $\mathcal{K}_{+2}^{(0)}(\infty)$ and $\mathcal{K}_{-2}^{(0)}(\infty)$, respectively,

$$\mathcal{K}_2^{(0)}(\infty)=\mathcal{K}_{+2}^{(0)}(\infty)+\mathcal{K}_{-2}^{(0)}(\infty)\ , \tag{3.37}$$
$$\mathcal{K}_{\pm 2}^{(0)}(\infty)=-\tfrac{1}{2}\int_0^{\infty}d\tau_1\langle[H_1^{(0)\times}(t),H_1^{(0)}\times(t-\tau_1)]_{\pm}\rangle\ ,$$

where $[X,Y]_{\pm}=XY\pm YX$. The integrand function of $\mathcal{K}_{+2}^{(0)}(\infty)$ $[\mathcal{K}_{-2}^{(0)}(\infty)]$ is an *even* [*odd*] function of τ_1.

This second-order approximation in $H_1^{(0)\times}(t)$ can be pursued further. The fourth-order approximation to Eq. (3.32) is

$$\frac{\partial}{\partial t}\langle A^{(0)}(t)\rangle=[\mathcal{K}_2^{(0)}(\infty)+\mathcal{K}_4^{(0)}(\infty)]\langle A^{(0)}(t)\rangle\ , \tag{3.38}$$

with

$$\mathcal{K}_4^{(0)}(\infty)=\int_0^{\infty}dt_1 k_4^{(0)}(t|t_1)-\int_0^{t}dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\{k_2^{(0)}(t|t_2)k_2^{(0)}(t_1|t_3)+k_2^{(0)}(t|t_3)k_2^{(0)}(t_1|t_2)\}\ , \tag{3.39}$$

where

$$\begin{aligned}k_4^{(0)}(t_1|t_4)=&\int_{t_4}^{t_1}dt_2\int_{t_4}^{t_2}dt_3\langle H_1^{(0)\times}(t_1)H_1^{(0)\times}(t_2)H_1^{(0)\times}(t_3)H_1^{(0)\times}(t_4)\rangle\\&-\langle H_1^{(0)\times}(t_1)H_1^{(0)\times}(t_2)\rangle\langle H_1^{(0)\times}(t_3)H_1^{(0)\times}(t_4)\rangle\ .\end{aligned} \tag{3.40}$$

The Markovian form of Eq. (3.32) deserves some comments.

The order-cumulant expansion (3.33) of $\mathcal{K}^{(0)}(t)$ is often employed in the limit of short correlation times τ_c. In fact, it can be proven that the order of magnitude of $\mathcal{K}_m^{(0)}(t)$ is $H_1^{(0)\times}(t)^m\tau_c^{m-1}$ and the series (3.33) is expected to converge for small values of the expansion parameter $H_1^{(0)\times}(t)\tau_c$. However, it must be pointed out that the smallness of the parameter $H_1^{(0)\times}(t)\tau_c$ is a *sufficient but not a necessary* condition in order to guarantee meaningfulness to Eq. (3.32). The basic requirement is the time scale separation between the dynamics of $\langle A^{(0)}(t)\rangle$ and $H_1^{(0)\times}(t)$. In I, cases have been presented where the expansion (3.33) has been extended to the region $H_1^{(0)\times}(t)\tau_c \gg 1$.

For later use we specialize $\mathcal{K}_2^{(0)}(\infty)$ in Eq. (3.34) to the usual case

$$H_{AB}=\sum_{\alpha}\Omega_{\alpha}(\mathbf{W})A_{\alpha}\ , \tag{3.41}$$

where A_α and $\Omega_\alpha(\mathbf{W})$ are an operator acting in the $\mathcal{A}$ space and a classical function of the stochastic variable $\mathbf{W}$, respectively. A_α is not necessarily Hermitian, even if H_{AB} must be. This implies that in general $\Omega_\alpha(\mathbf{W})$ is complex. $\langle H_{AB}\rangle$ is supposed to vanish. Otherwise, the averaged value must be included in the definition of H_A. Let $|a\rangle\rangle$, $|b\rangle\rangle$, . . . be the eigenstates of H_A with energies $\omega_a,\omega_b,\ldots$. Equation (3.34) becomes

$$\frac{\partial}{\partial t}\langle A_{ab}^{(0)}(t)\rangle=\sum_{c,d}\mathcal{K}_{2_{abcd}}^{(0)}(\infty)\langle A_{cd}^{(0)}(t)\rangle\ , \tag{3.42}$$

where $X_{ab}=\langle\langle a|X|b\rangle\rangle$. By inspection it is seen that

$$\mathcal{K}_{2_{abcd}}^{(0)}(\infty)=\exp[i(\omega_{cd}-\omega_{ab})t]\mathcal{R}_{2_{abcd}}^{*}\ , \tag{3.43}$$

where $\omega_{nm}=\omega_n-\omega_m$ and $\mathcal{R}_{2_{abcd}}$ is a constant quantity for stationary stochastic processes (X^* is the complex conjugate of X). From Eq. (3.35), disentangling the double commutator in Eq. (3.36) gives

$$\mathcal{R}_{2_{abcd}}=-\sum_{\alpha,\beta}\int_0^{\infty}ds\,C_{\alpha\beta}(s)\left[\delta_{bd}\sum_n A_{an}^{\alpha}A_{nc}^{\beta}e^{i\omega_{cn}s}-A_{ac}^{\beta}A_{db}^{a}e^{i\omega_{ca}s}\right]+C_{\beta\alpha}(-s)\left[\delta_{ac}\sum_n A_{dn}^{\beta}A_{nb}^{\alpha}e^{i\omega_{nd}s}-A_{ac}^{\alpha}A_{db}^{\beta}e^{i\omega_{bd}s}\right]\ . \tag{3.44}$$

$C_{\alpha\beta}$ is the correlation function defined as

$$C_{\alpha\beta}(s)=\langle \Omega_\alpha(\tau+s)\Omega_\beta(\tau)\rangle \ . \tag{3.45}$$

In Eq. (3.42) only the terms $\langle A_{ab}^{(0)}(t)\rangle$ and $\langle A_{cd}^{(0)}(t)\rangle$ for which the inequality

$$|\omega_{ab}-\omega_{cd}| \ll 1/\Delta t \tag{3.46}$$

holds are significantly coupled to each other. This secular approximation reduces Eq. (3.42) to

$$\frac{\partial}{\partial t}\langle A_{ab}^{(0)}(t)\rangle=\sum_{c,d}^{(\mathrm{sec})} \exp[i(\omega_{cd}-\omega_{ab})t] \times \mathcal{R}^{*}_{2_{abcd}}\langle A_{cd}^{(0)}(t)\rangle \ , \tag{3.47}$$

where the sum is now limited to terms which obey Eq. (3.46). Combining back to the original representation yields

$$\frac{\partial}{\partial t}\langle A_{ab}(t)\rangle=i\omega_{ab}\langle A_{ab}(t)\rangle+\sum_{c,d}^{(\mathrm{sec})}\mathcal{R}^{*}_{2_{abcd}}\langle A_{cd}(t)\rangle \ . \tag{3.48}$$

Equation (3.48) shows that the time evolution of the system $\mathcal{A}$ is described on the coarse-grained scale Δt by a linear differential system with constant coefficients. On this scale the propagator G reduces to G^{CG} where

$$G^{\mathrm{CG}}(z)=\frac{|b_0)(b_0|}{z-(iH_A^{\times}+\mathcal{R}_2^{*})} \ . \tag{3.49}$$

G^{CG} is the effective propagator describing the dynamic behavior of slow atom states, namely, states of the system $\mathcal{A}$ relaxing on time scales T longer than the correlation time of the bath τ_c. The general properties of the superoperator $\mathcal{R}_2$ can be found in many textbooks [2,33,35]. Relevant to the present discussion is the identification

$$\begin{aligned}\mathcal{R}_{2_{aacc}}&=\Gamma_{c\to a}, \quad c\neq a \ ,\\ \mathcal{R}_{2_{aaaa}}&=-\sum_{n\neq a}\Gamma_{a\to n} \ ,\end{aligned} \tag{3.50}$$

where $\Gamma_{c\to a}$ expresses the transition rate from the level c to a of the atom system. According to Eq. (3.37), the relaxation matrix $\mathcal{R}_2$ can be separated in a Hermitian and an anti-Hermitian part $\mathcal{R}_{+2}$ and $\mathcal{R}_{-2}$, respectively,

$$\begin{aligned}\mathcal{R}_2&=\mathcal{R}_{+2}+\mathcal{R}_{-2} \ ,\\ \mathcal{R}_{\pm 2}&=-\tfrac{1}{2}\int_0^{\infty}d\tau_1\langle [H_1^{(0)\times}(\tau_1),H_1^{(0)\times}(0)]_{\pm}\rangle \ .\end{aligned} \tag{3.51}$$

$\mathcal{R}_{+2}$ describes all relaxation effects whereas $\mathcal{R}_{-2}$ provides a (usually much smaller) contribution describing frequency shifts. A useful property which can be proved by inspection is

$$\mathcal{R}_{\pm 2_{abcd}}=\pm\mathcal{R}^{*}_{\pm 2_{cdab}} \ , \tag{3.52}$$

which results in

$$\Gamma_{c\to a}=\Gamma_{a\to c} \ . \tag{3.53}$$

Equation (3.53) implies that at equilibrium the atom levels are equally populated. This is a consequence of the assumed classical character of the thermal bath. However, arguments based solely on bath *thermodynamics* imply the correct detailed-balance condition [37]

$$e^{-\hbar\omega_c/kT}\Gamma_{c\to a}=e^{-\hbar\omega_a/kT}\Gamma_{a\to c} \ . \tag{3.54}$$

A correct quantum-mechanical picture of the bath still recovers Eqs. (3.48) and (3.54) [13,33].

In order to gain insight into the role played by the slow atom states, let us take into consideration their effect on the atom-bath term by referring to the cases with $n=2,3$. The case $n=1$ is skipped since it is of limited interest for the present discussion.

For $n=2$ three possibilities are given: either the observable A, the intermediate state $|S_{k_2}^{\alpha_2},\sigma_2\rangle$, or both are slow. If the observable A is slow, the atom-bath term given by Eq. (3.18b) reduces to

$$\mathfrak{A}_{\{k_1,k_2\}}(i\bar{\omega})=\sum_{\alpha_1,\alpha_2=\pm 1}\sum_{\sigma_1,\sigma_2}\alpha_1\alpha_2\langle\rho_A|S_{k_2}^{\alpha_2}\sigma_2\rangle\langle\sigma_2,S_{k_2}^{\alpha_2}|\langle G[\bar{i}\omega+i\,\mathrm{sgn}(k_2)\omega_{k_2}]\rangle|S_{k_1}^{\alpha_1},\sigma_1\rangle \times\left\langle\sigma_1,S_{k_1}^{\alpha_1}\left|\frac{1}{i\bar{\omega}-(iH_A^{\times}+\mathcal{R}_2^{*})}\right|A\right\rangle \ . \tag{3.55}$$

The other two cases are obvious. In all cases the overall bath average of the atom-bath term with $n=2$ is factorized as a product of two bath averages. The slow variable is driven by the coarse-grained propagator G^{CG} [Eq. (3.49)].

The form of Eq. (3.55) deserves some comments. It can be rewritten as

$$\mathfrak{A}_{\{k_1,k_2\}}(i\bar{\omega})=-i\sum_{\alpha_1=\pm 1}\sum_{\sigma_1}\alpha_1\hat{\Phi}_{S_{k_2};S_{k_1}^{\alpha_1},\sigma_1}[i\bar{\omega}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]\hat{\psi}^{\mathrm{CG}}_{\sigma_1,S_{k_1}^{\alpha_1};A}(i\bar{\omega}) \ , \tag{3.56}$$

namely, the atom-bath term may be expressed as a weighted sum of the Laplace transform of two correlation functions [Eqs. (1.4), (3.22)]. The superscript in the ψ function signals that the time evolution is governed by the coarse-grained propagator G^{CG}. Inserting Eq. (3.56) into Eq. (2.32) provides the expression of the second-order susceptibility $\chi^{(2)}$. The reader is advised to compare this expression with $\chi^{(1)}$ [Eq. (1.3a)].

This generalization of the linear-response theory can be extended to higher orders. Anyway, by increasing the order n the vertices of the atom-bath term [Eqs. (2.23), (3.17)], i.e., the atom-radiation interaction acts, increase and a number

of different choices can be made in the design of the spectroscopy. This richness has as counterpart a more involved interpretation. This limitation steps in for $n=3$ and becomes more and more apparent for schemes with $n>3$. Nonetheless, for $n=3$ it is worth noting the case in which the first atom-radiation act sets the atom in a slow state. In this case the atom-bath term reads

$$\mathfrak{A}_{\{k_1,k_2,k_3\}}(i\bar{\omega})=-i\sum_{\alpha_1,\alpha_2=\pm1}\sum_{\sigma_1,\sigma_2}\alpha_1\alpha_2\hat{\Phi}_{S_{k_3};S_{k_2}^{\alpha_2},\sigma_2}[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]$$
$$\times\hat{\psi}^{\mathrm{CG}}_{\sigma_2,S_{k_2}^{\alpha_2};S_{k_1}^{\alpha_1},\sigma_1}[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}]\hat{\psi}_{\sigma_1,S_{k_1}^{\alpha_1};A}[i\bar{\omega}]\ . \tag{3.57}$$

Inserting Eqs. (3.56) and (3.57) in Eq. (2.32) delivers the expression of the nonlinear susceptibility $\chi^{(2)}$ and $\chi^{(3)}$. $\chi^{(2)}$ and $\chi^{(3)}$ extend in a natural way the form of the linear susceptibility $\chi^{(1)}$, in that they are related to a product of Laplace-transformed *equilibrium* correlation functions. The above derivation has put into evidence the critical role played by the presence of the slow states.

We conclude the present section by rewriting Eqs. (3.56) and (3.57) in a slightly different fashion, by replacing the response function Φ with the relaxation function Ψ. This replacement is desirable for applications. The response function involves a commutator [Eq. (1.4)] whereas if canonical equilibrium is assumed, the relaxation function is delivered by the simpler form [Eq. (1.5)] which can be directly interpreted as a correlation function. Resorting to Eq. (1.3) yields

$$\mathfrak{A}_{\{k_1,k_2\}}(i\bar{\omega})=-i\sum_{\alpha_1=\pm1}\sum_{\sigma_1}\alpha_1\{\chi_{0S_{k_2};S_{k_1}^{\alpha_1},\sigma_1}+i\beta[i\bar{\omega}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]\hat{\Psi}_{S_{k_2};S_{k_1}^{\alpha_1},\sigma_1}[i\bar{\omega}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]\}\hat{\psi}^{\mathrm{CG}}_{\sigma_1,S_{k_1}^{\alpha_1};A}(i\bar{\omega})\ , \tag{3.58}$$

$$\mathfrak{A}_{\{k_1,k_2,k_3\}}(i\bar{\omega})=-i\sum_{\alpha_1,\alpha_2=\pm1}\sum_{\sigma_1,\sigma_2}\alpha_1\alpha_2\{\chi_{0S_{k_3};S_{k_2}^{\alpha_2},\sigma_2}+i\beta[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]$$
$$\times\hat{\Psi}_{S_{k_3};S_{k_2}^{\alpha_2},\sigma_2}[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}+i\,\mathrm{sgn}(k_2)\omega_{k_2}]\}$$
$$\times\hat{\psi}^{\mathrm{CG}}_{\sigma_2,S_{k_2}^{\alpha_2};S_{k_1}^{\alpha_1},\sigma_1}[i\bar{\omega}+i\,\mathrm{sgn}(k_1)\omega_{k_1}]\hat{\psi}_{\sigma_1,S_{k_1}^{\alpha_1};A}[i\bar{\omega}]\ . \tag{3.59}$$

Extensive experimental studies of second- and third-order nonlinear spectroscopies with slow atom states have been carried out for a long time [29,30]. Both slow observables and slow intermediate states have been observed and may be dealt with by Eqs. (3.56)–(3.59). In those papers the bath effects were accounted for by a Bloch theory. The present approach shed light on the good agreement which is found between that rough relaxation theory and the experimental findings about the relaxation of the slow states. The basic motivation lies in the fact that the relaxation of slow atom states is accounted for by Bloch relaxation times, as widely detailed in I.

In the next section a fairly general model of the system $\mathcal{A}$ is presented. Section V will discuss in detail the case of a second-order spectroscopy (the case with $n=3$ is postponed to a later paper).

IV. MODELING THE SYSTEM $\mathcal{A}$

This section is devoted to modeling the system $\mathcal{A}$. The plan is identical to the one presented in I. We start by assuming $\mathcal{A}$ to be a two-level system (TLS). This allows us to make clearer some features of the nonlinear response. Then, in order to ensure a satisfactory level of generality, we address ourselves to multilevel systems. The system $\mathcal{A}$ will be modeled as a particle with spin $S=\frac{1}{2}$ interacting with a second particle with arbitrary spin I. After a general discussion, examples will be drawn for the case $I=\frac{1}{2}$ (four-level system: FLS).

The atom and atom-bath Hamiltonians to be specified in Eq. (3.12) are assumed to be of the general form

$$H_A=\omega_0 S_z+\omega_I S_z I_z\ , \tag{4.1a}$$

$$H_{AB}(\mathbf{W})=\underline{\omega}(\mathbf{W})\cdot\underline{S}+\underline{S}\cdot\underline{\underline{\omega}}(\mathbf{W})\cdot\underline{I}$$
$$=\sum_{k=x,y,z}\omega_k(\mathbf{W})S_k+\sum_{kl=x,y,z}\omega_{kl}(\mathbf{W})S_k I_l\ . \tag{4.1b}$$

ω_0 and ω_I are scalar quantities. $\underline{\omega}(\mathbf{W})$ and $\underline{\underline{\omega}}(\mathbf{W})$ are a vector and a matrix with elements $\omega_k(\mathbf{W})$, $k=x,y,z$, and $\omega_{kl}(\mathbf{W})$, $k,l=x,y,z$, respectively, depending on the stochastic variable $\mathbf{W}$. In a magnetic resonance experiment ω_0 and ω_I coincide with the Larmor ($\omega_0=\gamma\mathcal{H}_0$, $\mathcal{H}_0$ being the static magnetic field) and hyperfine frequency, respectively. $\mathcal{H}_0$ defines the z axis. It is assumed that

$$\langle\omega_k(\mathbf{W})\rangle=\langle\omega_{kl}(\mathbf{W})\rangle=0\ , \tag{4.2}$$

yielding $\langle H_{AB}(\mathbf{W})\rangle=0$. The case $\langle H_{AB}(\mathbf{W})\rangle\neq0$ can be handled by including the averaged value in H_A. As in I, the discussion will be limited to the region

$$\beta^{-1}>\omega_0>\omega_I,\quad\langle\omega_k^2(\mathbf{W})\rangle^{1/2},\quad\langle\omega_{kl}^2(\mathbf{W})\rangle^{1/2}\ . \tag{4.3}$$

The rms amplitude of the fluctuating fields $\langle\omega_k^2(\mathbf{W})\rangle^{1/2}$,

$\langle \omega_{kl}^2(\mathbf{W}) \rangle^{1/2}$ is a central quantity governing the relaxation property of the observable of interest (see I). Henceforth its order of magnitude will be referred to as Δ. In the next section the explicit form of the coarse-grained propagator G^{CG} [Eq. (3.49)] is discussed for the present model.

A. Relaxation properties of the slow atom states

The discussion is split into two parts dealing with the cases of two-level and multilevel systems, respectively. The coarse-grained time scale Δt will always be assumed to be larger than $1/\omega_0$. Two motivations are adduced. First, a number of physical systems of current interest exhibit fluctuation phenomena with correlation times τ_c longer than $1/\omega_0$. Furthermore, while for τ_c longer than $1/\omega_0$ a *single* slow atom state will be seen to be present, for τ_c comparable to or shorter than $1/\omega_0$, the fluctuations are so fast as to favor the emergence of a *set* of slow atom states, according to the model Hamiltonian [Eq. (4.1)]. To gain insight into the role of slow atom states, this appears to be an inessential complication.

With a view to helping the reader during the following discussion, the mutual position of the resonances of the atom, the bandwidth $1/\Delta t$ covered by the coarse-grained procedure, and the rates of the atom relaxation processes are illustrated by Fig. 3. Some of the quantities will be introduced below.

1. Two-level structure

For a TLS there is only a resonance frequency ω_0. The spin S spans states which are superpositions of

$$S_0 = S_z \ , \qquad S_\pm = S_x \pm i S_y \ . \tag{4.4}$$

The eigenstates of H_A are

$$H_A |\pm\rangle\rangle = \pm \frac{\omega_0}{2} |\pm\rangle\rangle \ . \tag{4.5}$$

On the scale $\Delta t \gg 1/\omega_0$ (Fig. 3, top), according to Eqs. (3.46) and (3.50), Eq. (3.48) reduces to

$$\frac{\partial}{\partial t}\langle A_{++}(t)\rangle = -\Gamma_{+\to-}\langle A_{++}(t)\rangle + \Gamma_{-\to+}\langle A_{--}(t)\rangle \ , \tag{4.6a}$$

$$\frac{\partial}{\partial t}\langle A_{--}(t)\rangle = -\Gamma_{-\to+}\langle A_{--}(t)\rangle + \Gamma_{+\to-}\langle A_{++}(t)\rangle \ , \tag{4.6b}$$

$$\frac{\partial}{\partial t}\langle A_{+-}(t)\rangle = (i\omega_0 + \mathcal{R}^*_{2_{+-+-}})\langle A_{+-}(t)\rangle \ . \tag{4.6c}$$

By the above equations and Eq. (3.52), one derives the relevant ψ functions (a shorthand notation is introduced)

$$\hat{\psi}_z^{CG}(z) \equiv \langle S_z | \langle G^{CG}(z)\rangle | S_z \rangle = \frac{1}{4}\frac{1}{z + T_1^{-1}} \ , \tag{4.7a}$$

$$\hat{\psi}_+^{CG}(z) \equiv \langle S_+ | \langle G^{CG}(z)\rangle | S_+ \rangle = \frac{1}{2}\frac{1}{z - i(\omega_0 + \Delta\omega) + T_2^{-1}} \ , \tag{4.7b}$$

$$\hat{\psi}_-^{CG}(z) \equiv \langle S_- | \langle G^{CG}(z)\rangle | S_- \rangle = \frac{1}{2}\frac{1}{z + i(\omega_0 + \Delta\omega) + T_2^{-1}} \ , \tag{4.7c}$$

where the scalar product defined by Eq. (3.14) reduces to a trace over spin states and the usual relaxation times and dynamical shifts are defined as

$$T_1^{-1} = \Gamma_{+\to-} + \Gamma_{-\to+} = 2\Gamma_{+\to-} \ , \tag{4.8}$$

$$T_2^{-1} = -\mathrm{Re}\{\mathcal{R}_{2_{+-+-}}\} = -\mathrm{Re}\{\mathcal{R}_{+2_{+-+-}}\} \ , \tag{4.9}$$

$$\Delta\omega = -\mathrm{Im}\{\mathcal{R}_{2_{+-+-}}\} = -\mathrm{Im}\{\mathcal{R}_{-2_{+-+-}}\} \ . \tag{4.10}$$

ψ^{CG} correlation functions other than Eq. (4.7) vanish on the coarse-grained scale $\Delta t \gg 1/\omega_0$. It must be noted that in the high-temperature limit $\beta\omega_0 < 1$, the Ψ correlation functions [Eq. (1.5)] reduces to

$$\Psi \cong \tfrac{1}{2}\psi \ . \tag{4.11}$$

2. Multilevel structure

In the multilevel system described by the model Hamiltonian [Eq. (4.1)] with $I \neq 0$, the coarse-grained scale Δt, defined in Sec. III C by demanding $\tau_c \ll \Delta t \ll T_A$, can be chosen with different levels of accuracy (Fig. 3). *High accuracy requires that* $\Delta t \equiv \Delta t_H < 1/\omega_I$. The opposite choice $\Delta t \equiv \Delta t_L > 1/\omega_I$ implies *low* accuracy. *Improved low accuracy must ensure* $\Delta t_I > \Delta t_L > 1/\omega_I$, *where* Δt_I^{-1} *is the order of magnitude of the* intermultiplet relaxation rates (a multiplet is a set of levels characterized by the *same* electron spin state). In many systems of interest the value of the hyperfine constant ω_I is larger than T_A. So, the discussion will be essentially limited to the relaxation effects still present on the coarse-grained scale Δt_L, even if some insight in the relaxation regime occurring on Δt_H will be provided.

Let us consider the three subspaces of the states of the system $\mathcal{A}$ given by

$$\mathcal{A}_\mu \equiv \{ |S_\mu, P_m\rangle ; \mu = 0, \pm 1, m = -I, -I+1, \ldots, I-1, I \}, \tag{4.12}$$

where S_μ are defined in Eq. (4.4) and P_m denotes the projector on the eigenvector of I_z with eigenvalue m. The scalar product [Eq. (3.14)] for the system $\mathcal{A}$ requires tracing over both the states S and I. Note that

$$\mathcal{A} \neq \mathcal{A}_1 \oplus \mathcal{A}_0 \oplus \mathcal{A}_{-1} \ . \tag{4.13}$$

The subspace $\mathcal{A}_\mu$ is *invariant* on the coarse-grained time scale $\Delta t_L > 1/\omega_I$, according to Eq. (3.48). In fact, Eq. (3.46) with $\Delta t = \Delta t_L > 1/\omega_I$ implies

$$\omega_{ab} = \omega_{cd} \ . \tag{4.14}$$

Invariance of $\mathcal{A}_\mu$ is equivalent to saying in the

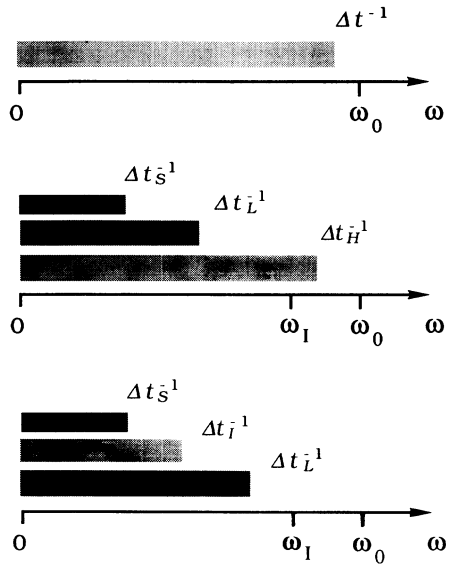

FIG. 3. Mutual positions of the resonances of the atom, the bandwidth $1/\Delta t$ covered by the coarse-grained procedure, and the rates of the atom relaxation processes. ω_0 is the Zeeman splitting, ω_I is the hyperfine splitting of the $2I+1$ levels forming each multiplet. Δt_s^{-1}, Δt_I^{-1} are the order of magnitude of the intermultiplet and intramultiplet relaxation rates, respectively. Δt is the time interval on which coarse graining is carried out. Top: TLS case. Middle: FLS case, high accuracy $\Delta t_H^{-1} > \omega_I$ vs low accuracy $\Delta t_L^{-1} < \omega_I$. Bottom: FLS case, improved low accuracy $\Delta t_L^{-1} > \Delta t_I^{-1}$. See text for details.

Schrödinger picture that (i) electron coherences and populations do not mix together while time passes, and (ii) nuclear coherences are not effective on the scale $\Delta t = \Delta t_L > 1/\omega_I$. The observable A of the spectroscopy may usually be expressed as a linear combination of states belonging to $\mathcal{A}_\mu$ (for example, in electron spin resonance the observable is the electron magnetization).

Let us analyze first the relaxation of the states of the subspace $\mathcal{A}_0$ which will be referred to as the population subspace. The eigenstates of H_A are

$$H_A|\pm,m\rangle\rangle = \left[\pm\frac{\omega_0}{2}+m\omega_I\right]|\pm,m\rangle\rangle = \omega_{\pm m}|\pm,m\rangle\rangle \tag{4.15}$$

and in the subspace $\mathcal{A}_0$ Eq. (3.48) reduces to the rate equation [$\langle A_\alpha(t)\rangle \equiv \langle A_{\alpha\alpha}(t)\rangle$]

$$\begin{aligned}\frac{\partial}{\partial t}\langle A_{\pm m}(t)\rangle = &-\sum_{k\,(\neq m)}\Gamma_{\pm m\to\pm k}\langle A_{\pm m}(t)\rangle \\ &+\sum_{k\,(\neq m)}\Gamma_{\pm k\to\pm m}\langle A_{\pm k}(t)\rangle \\ &-\sum_k\Gamma_{\pm m\to\mp k}\langle A_{\pm m}(t)\rangle \\ &+\sum_k\Gamma_{\mp k\to\pm m}\langle A_{\mp k}(t)\rangle\ .\end{aligned} \tag{4.16}$$

Equation (4.16) yields the general form of the $2(2I+1)$ coupled differential equations governing the time evolution of $\langle A_{\pm m}(t)\rangle$. Some features of the solution of the above system deserve consideration. First of all we note that [Eqs. (3.44), (3.50), (4.3)]

$$\frac{\Gamma_{\pm m\to\pm k}}{\Gamma_{\pm m\to\mp k}} \approx \frac{\tau_c}{1+\omega_I^2\tau_c^2}\Big/\frac{\tau_c}{1+\omega_0^2\tau_c^2} \gg 1, \quad \tau_c \gg \omega_0^{-1}\ . \tag{4.17}$$

Equation (4.17) assumes that the magnitudes of the random fields contributing to $\Gamma_{\pm m\to\pm k}$ and $\Gamma_{\pm m\to\mp k}$ are comparable and shows that, provided that $\tau_c \gg \omega_0^{-1}$, the transition probability between states with *opposite* spin is fairly smaller than the transition probability between states with *same* spin.

Two time scales in the relaxation of the system $\mathcal{A}$ are then identified (Fig. 3): A first scale $\Delta t_I \approx 1/\Gamma_{\pm m\to\pm k}$ on which $\langle A_{\pm m}(t)\rangle$ relaxes due to couplings with elements $\langle A_{\pm k}(t)\rangle$ with $k\neq m$ belonging to the same multiplet, and a second scale $\Delta t_S \approx 1/\Gamma_{\pm m\to\mp k} \gg \Delta t_I$ on which $\langle A_{\pm m}(t)\rangle$ relaxes due to couplings with elements $\langle A_{\mp k}(t)\rangle$ belonging to the other multiplet.

The low-accuracy coarse graining occurs on the scale $\Delta t_L > 1/\omega_I$. On the other hand, it is required that $\Delta t_L \ll \Delta t_S$. Improving the accuracy requires $\Delta t \ll \Delta t_I \ll \Delta t_S$. The identification $\Delta t = \Delta t_L$ may be questionable in that sometimes $\Delta t_I \approx \omega_I^{-1}$. In Fig. 3 (bottom) this identification is presumed.

Let us analyze the requirement $\Delta t_L \ll \Delta t_S$. If Δ is the order of magnitude of the random fields $\langle\omega_k^2(\mathbf{W})\rangle^{1/2}$, $\langle\omega_{kl}^2(\mathbf{W})\rangle^{1/2}$, it comes out that

$$\Delta t_S \approx \frac{1}{\Gamma_{\pm m\to\mp k}} \approx \left[\frac{\Delta^2\tau_c}{1+\omega_0^2\tau_c^2}\right]^{-1} > \frac{\omega_0}{\Delta^2}\ . \tag{4.18}$$

Δt_L may be chosen to be much less than Δt_S, if

$$\Delta^2/\omega_0\omega_I \ll 1\ . \tag{4.19}$$

Moreover, in the limit of long correlation times $\tau_c > 1/\omega_0$, which represent the region of prominent interest of the present paper,

$$\Delta t_S \approx \omega_0^2\tau_c/\Delta^2 \tag{4.20}$$

and then the inequality

$$\Delta^2/\omega_0^2\omega_I\tau_c < 1 \tag{4.21}$$

implies that Δt_L may be chosen so that $\Delta t_L \ll \Delta t_S$.

Both Eqs. (4.19) and (4.21) do not follow directly from Eq. (4.3). Nonetheless the additional limitations that are imposed on the range of the parameters are rather weak, since the leading factor of Eqs. (4.19) and (4.21) is the ratio Δ/ω_0 which is usually much less than one. For example, in many practical cases either $\Delta \approx \omega_I$ or $\omega_I\tau_c > 1$, then Eq. (4.3) implies Eqs. (4.19) and (4.21), respectively.

We start to analyze the solution of the system of Eqs. (4.16) on the scale Δt_L, henceforth assumed to be shorter than Δt_S. For the moment the accuracy is assumed low and let $\Delta t_L \gg \Delta t_I$. On this scale, at any time t, the following equation holds:

$$\sum_{k\,(\neq m)} \Gamma_{\pm m\to\pm k}\langle A_{\pm m\pm m}(t)\rangle = \sum_{k\,(\neq m)} \Gamma_{\pm k\to\pm m}\langle A_{\pm k\pm k}(t)\rangle \ . \tag{4.22}$$

Equation (4.22) states that on the scale $\Delta t_L \gg \Delta t_I$ each multiplet rearranges instantaneously and Eq. (4.16) reduces to

$$\frac{\partial}{\partial t}\langle A_{\pm m\pm m}(t)\rangle = -\sum_k \Gamma_{\pm m\to\mp k}\langle A_{\pm m\pm m}(t)\rangle + \sum_k \Gamma_{\mp k\to\pm m}\langle A_{\mp k\mp k}(t)\rangle \ . \tag{4.23}$$

With a view to solving Eq. (4.23) we write the solution as

$$\langle A_{\pm m\pm m}(t)\rangle = a_\pm(t)\exp[-\beta\omega_{\pm m}] \ . \tag{4.24a}$$

$a_\pm(t)$ is a function to be determined. $\langle A_{\pm m\pm m}(t)\rangle$ in the form of Eq. (4.24a) fits in Eq. (4.22). Equation (4.22) states that on the scale $\Delta t_L \gg \Delta t_I$ the multiplets are in *internal* equilibrium but not in equilibrium with respect to each other. The exponential factor of Eq. (4.24a) meets the detailed balance [Eq. (3.54)]. However, the stochastic frame implies that transition probabilities are related by Eq. (3.53). The correction is irrelevant in the frame of the high-temperature approximation [Eq. (4.3)]. So, henceforth we approximate

$$\langle A_{\pm m\pm m}(t)\rangle \cong a_\pm(t) \tag{4.24b}$$

and assume Eq. (3.53). By replacing Eq. (4.24b) in Eq. (4.23) and summing up the index m we obtain [$a_+(t)+a_-(t)=\mathrm{Tr}\{A\}=0$ for states belonging to $\mathcal{A}_0$]

$$\frac{\partial}{\partial t}a_\pm(t) = -\frac{1}{T_1}a_\pm(t) \ , \tag{4.25}$$

where

$$\frac{1}{T_1} = \frac{1}{2I+1}\sum_{m,k}(\Gamma_{+k\to-m}+\Gamma_{-m\to+k}) \ . \tag{4.26}$$

Equation (4.26) states that on the scale $\Delta t_L \gg \Delta t_I$ the decay of the ensemble averaged matrix elements $\langle A_{\pm m\pm m}(t)\rangle$ occurs with a *single* exponential law whose time constant is T_1. It must be noted that in I $1/T_{12}$ is expressed by a much more involved formula [Eq. (104)]. The full equivalence between the two expressions has been proven [42].

Now, Eq. (3.22) becomes

$$\hat{\psi}^{\mathrm{CG}}_{zm}(z) \equiv \langle S_z P_m | \langle G^{\mathrm{CG}}(z)\rangle | S_z P_m\rangle = \frac{1}{4(2I+1)}\frac{1}{z+T_1^{-1}} \ . \tag{4.27}$$

According to the definition of $\hat{\psi}^{\mathrm{CG}}_z$ [Eq. (4.7a)], it is found that

$$\hat{\psi}^{\mathrm{CZ}}_z(z) = \frac{1}{4}\frac{1}{z+T_1^{-1}} \ , \tag{4.28}$$

which is formally identical to the related expression for a TLS [Eq. (4.7a)].

A more accurate view of the relaxation process is delivered by the improved low accuracy (Fig. 3, bottom) which requires $\Delta t_L \ll \Delta t_I \ll \Delta t_S$.

On this scale a transient is present for time shorter than T_1 accounting for the rearrangements of the multiplets towards *internal* equilibrium [note that on the enlarged scale $\Delta t_L \gg \Delta t_I$ the rearrangements occur instantaneously, see Eq. (4.22)]. For $t < T_1$ the time evolution of the transient is governed by

$$\frac{\partial}{\partial t}\langle A_{\pm m\pm m}(t)\rangle = -\sum_{k\,(\neq m)} \Gamma_{\pm m\to\pm k}\langle A_{\pm m\pm m}(t)\rangle + \sum_{k\,(\neq m)} \Gamma_{\pm k\to\pm m}\langle A_{\pm k\pm k}(t)\rangle \ , \tag{4.29}$$

which is derived by neglecting the second line of Eq. (4.16).

The general solution of Eq. (4.16) is expressed as a sum of $2(2I+1)$ decaying exponentials with eigenvalues 0, $1/T_1$, and γ_k ($k=1,\ldots,4I$). Due to Eq. (4.17), $\gamma_k \ll 1/T_1$. The most general expression of the ψ function is

$$\hat{\psi}^{\mathrm{CG}}_{z\,mm'}(z) \equiv \langle S_z P_m | \langle G^{\mathrm{CG}}(z)\rangle | S_z P_{m'}\rangle = \frac{c_0}{z} + \frac{c_1}{z+1/T_1} + \sum_{k=1}^{4I}\frac{c_{k+1}}{z+\gamma_k} \ , \tag{4.30}$$

where c_i is a constant. For stochastic models $c_0=0$.

A relevant observable belonging to $\mathcal{A}_0$ is $A=S_z$, i.e., the component of the magnetization parallel to the static magnetic field $\mathcal{H}_0$. In I the show character of $\langle S_z(t)\rangle$ has been extensively studied, by resorting to the correlation function

$$\bar{S}_z(t) = \frac{\beta\omega_0}{2(2I+1)}\mathrm{Tr}_{\{S,I\}}\{\langle S_z S_z(t)\rangle\} = \frac{\beta\omega_0}{2(2I+1)}\mathrm{Tr}_{\{S,I\}}\{S_z\langle S_z(t)\rangle\} = \frac{\beta\omega_0}{2(2I+1)}\psi_z(t) \ . \tag{4.31}$$

$\bar{S}_z(t)$ can be interpreted as the relaxation of the magnetization after it has been prepared by upsetting it from the value at thermal equilibrium (directed along the static magnetic field $\mathcal{H}_0$, see I for details).

It was proved that (i) on the scale Δt ($T_1 \gg \Delta t \gg \tau_c$) $\bar{S}_z(t)$ relaxes as a single exponential with time constant given by T_1, and (ii) the time scale separation ($T_1 \gg \tau_c$) is ensured, i.e., $\langle S_z(t)\rangle$ is slow, on the sole basis of small amplitude of the fluctuating fields [Eq. (4.3)]. The constraint is mild, since it is *independent* of τ_c. In I these findings were derived by assuming either dichotomic correlated or Gaussian uncorrelated fluctuations. Nonetheless, to date, they have been extended also to uncorrelated dichotomic and correlated Gaussian fluctuations [43].

In order to complete the discussion let us turn to the

relaxation behavior of slow states belonging to the subspaces $\mathcal{A}_{\pm 1}$.

From I we know that, differently from ψ_z, the relaxation of ψ_x and ψ_y exhibits time scale separation only for short values of the correlation time τ_c, more precisely if $\Delta\tau_c \ll 1$, where Δ is the order of magnitude of the fluctuating fields. This implies that the slow character of atom states belonging to $\mathcal{A}_{\pm 1}$ (for example, S_x and S_y) is less strong than for states belonging to $\mathcal{A}_0$.

On the coarse-grained scale $\Delta t = \Delta t_L > 1/\omega_1$ (low accuracy), according to Eq. (4.14), Eq. (3.48) reduces to

$$\frac{\partial}{\partial t}\langle A_{\mp m \pm m}(t)\rangle = [\mp i(\omega_0 + m\omega_I) + \mathcal{R}^{*}_{\mp m,\pm m,\mp m,\pm m}] \times \langle A_{\mp m \pm m}(t)\rangle \tag{4.32}$$

and

$$\hat{\psi}^{\mathrm{CG}}_{\pm m}(z) \equiv \langle S_{\pm} P_m | \langle G^{\mathrm{CG}}(z)\rangle | S_{\pm} P_m \rangle = \frac{1}{2(2I+1)} \frac{1}{z \mp i(\omega_0 + m\omega_I + \Delta\omega_m) + 1/T_2^m} , \tag{4.33}$$

where, according to Eq. (3.50),

$$1/T_2^m = -\mathrm{Re}\{\mathcal{R}_{2_{+m,-m,+m,-m}}\} = -\mathrm{Re}\{\mathcal{R}_{2_{-m,m,-m,+m}}\} , \tag{4.34}$$

$$\Delta\omega_m = -\mathrm{Im}\{\mathcal{R}_{2_{+m,-m,+m,-m}}\} = -\mathrm{Im}\{\mathcal{R}_{2_{-m,m,-m,+m}}\} . \tag{4.35}$$

In Eq. (4.34) [Eq. (4.35)] only $\mathcal{R}_+$ ($\mathcal{R}_-$) contributes. Low-accuracy coarse graining requires $1/T_2^m \ll \omega_I$. For sufficiently long correlation times $T_2^{-1}(m)$ ($\approx \Delta^2\tau_c$) becomes comparable to the spacing ω_I and $\hat{\psi}^{\mathrm{CG}}_{\pm m}(i\omega)$ with different values of m start to overlap and merge together. In this region high accuracy is needed and one must put $\Delta t = \Delta t_H < 1/\omega_I$. In cases of interest the spectral overlap is a precursor of the breakdown of the time scale separation occurring at $T_2^{-1}(m) \approx \tau_c$, i.e., $\Delta^2\tau_c^2 \approx 1$. In the region $T_2^{-1}(m) < \tau_c$, the treatment of overlapping spectra can still be carried out in the framework of E.q (3.48). However, states of the subspaces $\mathcal{A}_{\pm 1}$ with different m are now coupled to each other, causing $\hat{\psi}^{\mathrm{CG}}_{\pm m}(i\omega)$ to be described by a sum of Lorentzians. We skip the detailed analysis of this case, which is secondary to the purposes of the present paper.

Finally, we note that, due to the high-temperature approximation [Eq. (4.3)], the relationship between the ψ function and the Ψ function is

$$\Psi \cong \frac{1}{2(2I+1)}\psi . \tag{4.36}$$

V. NONLINEAR RESPONSE OF TWO- AND FOUR-LEVEL SYSTEMS

In this section illustrations of the above findings will be presented by analyzing in detail an example of second-order nonlinear spectroscopy whose scheme involves slow atom states. The slow state is precisely the observable $A = S_z$.

As representative of second-order spectroscopies we choose the longitudinally detected electron spin resonance (LODESR) spectroscopy [29]. In a LODESR experiment (Fig. 4) two microwave fields act on the sample S. The fields, which are linearly polarized at right angles with respect to the applied static magnetic field B_0, have angular frequencies ω_1, ω_2 and amplitude B_1, B_2. The directions of the microwave fields and B_0 define the x and the z axis, respectively. The nonlinear character of the response of the spin system to the external fields is exposed by the presence of a signal at frequency $|\omega_1 - \omega_2|$ in the z component of the magnetization. This component can be phase detected by a coil C with axis parallel to B_0, so we identify the observable A with S_z.

Apart from the zero-frequency (static) term χ_0, the first nontrivial contribution to the LODESR susceptibility is $\chi^{(2)}$. In fact, due to the polarization of the two external fields, the angular-momentum conservation law makes $\chi^{(1)}$ virtually vanish, namely, no *linear* response is observed. Small contributions to $\chi^{(1)}$ come from angular-momentum exchange processes [driven by the bath fluctuations due to terms proportional to $S_{x,y}$ in Eq. (4.1b)]. In the absence of them, namely, if the system $\mathcal{A}$ exchanges angular momentum solely with the radiation, one finds exactly $\chi^{(1)} = 0$.

By increasing the amplitude of B_1, B_2, other contributions to the susceptibility such as $\chi^{(4)}, \ldots, \chi^{(2n)}$ appear, enriching with harmonics the response frequency spectrum. For example, in the low-frequency portion of the spectrum the harmonics of $|\omega_1 - \omega_2|$ are observed. However, the amplitudes B_1, B_2 are maintained small, so henceforth we will be concerned with $\chi^{(2)}$. With $A = S_z$ Eq. (1.7) yields

$$\Delta S_z(t) = B_1 B_2 \mathrm{Re}\{[\chi^{(2)}(\omega_1, -\omega_2) + \chi^{(2)}(-\omega_2, \omega_1)] \times \exp[i(\omega_1 - \omega_2)t] + [\chi^{(2)}(-\omega_1, \omega_2) + \chi^{(2)}(\omega_2, -\omega_1)] \times \exp[i(\omega_2 - \omega_1)t]\} . \tag{5.1}$$

Equation (5.1) describes the low-frequency part of the response. High-frequency contributions at frequency $\omega_1 + \omega_2$ are neglected. It can be easily shown that the second line of Eq. (5.1) is the complex conjugate of the first one. The discussion of Sec. II and particularly Eq. (2.32) allow us to relate the susceptibility to the underlying atom-radiation interaction process. For example, $\chi^{(2)}(\omega_1, -\omega_2)$ pertains to a process involving first the emission of an ω_1 photon followed by the absorption of a photon ω_2. Due to the phase detection of the signal, the recorded line shape is proportional to the amplitude of $\Delta S_z(t)$, expressed by its modulus $|\Delta S_z|$,

$$|\Delta S_z| = B_1 B_2 |\chi^{(2)}(\omega_1, -\omega_2) + \chi^{(2)}(-\omega_2, \omega_1)| = \gamma^2 B_1 B_2 |\mathrm{Tr}_{\{\mathcal{A}\}}(\rho_A S_x^{\times}\{\langle G(-i\omega_2) S_x^{\times} G[i(\omega_1 - \omega_2)]\rangle + \langle G(i\omega_1) S_x^{\times} G[i(\omega_1 - \omega_2)]\rangle\} S_z)| . \tag{5.2}$$

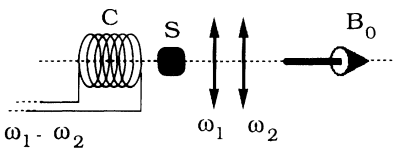

FIG. 4. Block scheme of the LODESR spectroscopy. C is the detecting coil, S is the sample, $\omega_{1,2}$ the frequencies of the two microwaves. B_0 is the static magnetic field.

The second equivalence follows from Eqs. (2.23) and (2.32) (both the microwave fields are along the x axis). To proceed further we must expand each vertex of the atom-bath term. According to Eq. (3.15),

$$S_x^{\times} = \sum_{\sigma} |S_y + iS_z, \sigma\rangle\langle\sigma, S_y + iS_z| - |S_y - iS_z, \sigma\rangle\langle\sigma, S_y - iS_z| , \tag{5.3}$$

where the set σ denotes a complete set of $(2I+1)\times(2I+1)$ operators in the space of the spin I. Insertion of Eq. (5.3) in Eq. (5.2) and straightforward rearrangements lead to the final expression in terms of the matrix elements of the propagator $G(z)$. The general expression is rather involved and will not be reported here.

Profiting from the slow character of the observable S_z very compact expressions are derived. Preliminarily, we remark that

$$\hat{\Psi}_{X,S_z}(\pm i\omega_{1,2}) \approx 0 , \tag{5.4}$$

where X is a generic atom state. Equation (5.4) asserts that the spectrum of $\langle \hat{S}_z(i\omega)\rangle$ does not extend up to frequencies of about $\omega_{1,2}$, namely, that

$$T_1^{-1} \ll \omega_{1,2} . \tag{5.5}$$

Since $\langle S_y \rangle = 0$, it follows that

$$\chi_{0S_x;S_x,\sigma} = 0 . \tag{5.6}$$

Furthermore

$$\left| \frac{i\omega_{1,2}\hat{\Psi}_{S_x;S_y,\sigma}(i\omega_{1,2})}{\chi_{0S_x;S_y,\sigma}} \right| \approx \frac{\omega_{1,2}}{\Delta\Omega} \gg 1 , \tag{5.7}$$

where $\Delta\Omega$ means the spectral extension of $\hat{\Psi}_{S_x;S_y,\sigma}$ around ω_0. The inequality follows from Eq. (4.3).

In I it was proved that under the sole hypothesis [Eq. (4.3)] $\langle S_z(t)\rangle$ is slow. Accordingly, in Eq. (5.2) the susceptibilities may be evaluated by resorting to the expression Eq. (3.58) for the atom-bath term. In the light of Eqs. (5.4)–(5.7), on the scale $\Delta t_L \gg \Delta t_1$ Eq. (5.2) reduces to

$$\begin{aligned} |\Delta S_z| &= \gamma^2 B_1 B_2 |\chi^{(2)}(\omega_1, -\omega_2) + \chi^{(2)}(-\omega_2, \omega_1)| \\ &= \beta\gamma^2 B_1 B_2 |\omega_1 \hat{\Psi}_{xy}(i\omega_1) - \omega_2 \hat{\Psi}_{xy}(-i\omega_2)| \\ &\quad \times |\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1 - \omega_2)]| , \end{aligned} \tag{5.8}$$

where $\Psi_{xy} \equiv \Psi_{S_x,S_y}$ and, due to Eq. (4.28),

$$|\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1 - \omega_2)]| = \frac{1}{4} \frac{1}{\sqrt{(\omega_1 - \omega_2)^2 + T_1^{-2}}} . \tag{5.9}$$

One of the main aims of the present paper is to elucidate the relationship between the nonlinear response and the relaxation properties of selected observables. In Sec. III C we have pointed out the role of slow variables to provide a "natural" extension to the relationship between *linear* susceptibility and *equilibrium* correlation function [Eq. (1.3)]. This relationship is stated by Eqs. (3.58) and (3.59) for the second- and third-order susceptibility in terms of products of Laplace transform of *equilibrium* correlation function. It is of remarkable experimental interest to investigate if, under proper conditions, the spectrum of the nonlinear susceptibility matches the spectrum of a single *equilibrium* correlation function. It will be shown that, under the sole basis of Eq. (4.3), the signal of the LODESR spectroscopy reproduces the spectrum of $\hat{\psi}_z^{\mathrm{CG}}$ in the regime $\omega_0\tau_c \gg 1$.

Let us discuss first the case of *fast* fluctuations, namely, $\omega_0^{-1} \ll \tau_c \ll \Delta^{-1}$.

For a TLS, on the scale $\Delta t \gg \omega_0^{-1}$

$$\hat{\psi}_{xy} = -\frac{i}{4}(\hat{\psi}_+ - \hat{\psi}_-) . \tag{5.10}$$

On account of Eqs. (4.7) and (4.11), by deleting off-resonance contributions, Eq. (5.8) becomes

$$\begin{aligned} |\Delta S_z| &= \beta \frac{\gamma^2 B_1 B_2}{32} \frac{1}{\sqrt{(\omega_1 - \omega_2)^2 + T_1^{-2}}} \\ &\quad \times \left| \frac{\omega_1}{i(\omega_1 - \omega_0 - \Delta\omega) + T_2^{-1}} \right. \\ &\quad \left. + \frac{\omega_2}{i(\omega_0 + \Delta\omega - \omega_2) + T_2^{-1}} \right| , \end{aligned} \tag{5.11}$$

where Eqs. (4.8)–(4.10) provide the expressions of T_1^{-1}, T_2^{-1}, and $\Delta\omega$, respectively. Equation (5.11) coincides with Eq. 5 of Ref. [29] derived in the Bloch-like scheme.

For the multilevel case, Eqs. (4.28), (4.33) yield

$$\begin{aligned} |\Delta S_z| &= \beta \frac{\gamma^2 B_1 B_2}{32(2I+1)} \frac{1}{\sqrt{(\omega_1 - \omega_2)^2 + T_1^{-2}}} \\ &\quad \times \sum_{m=1}^{2I+1} \left| \frac{\omega_1}{i(\omega_1 - \omega_0 - m\omega_I - \Delta\omega_m) + 1/T_2^m} \right. \\ &\quad \left. + \frac{\omega_2}{i(\omega_0 + m\omega_I + \Delta\omega_m - \omega_2) + 1/T_2^m} \right| . \end{aligned} \tag{5.12}$$

The parameters $1/T_2^m$ and $\Delta\omega_m$ are defined by Eqs. (4.34) and (4.35), respectively. It is interesting to note that, if $|\omega_1 - \omega_2|$ is less than T_2^{-1} for a TLS and the smallest of $1/T_2^m$ for a FLS, Eqs. (5.11) and (5.12) approach the limit form

$$|\Delta S_z| = \beta \frac{\gamma^2 B_1 B_2}{16} \frac{1}{\sqrt{(\omega_1-\omega_2)^2+T_1^{-2}}} \frac{\omega_1 T_2^{-1}}{(\omega_1-\omega_0)^2+T_2^{-2}}, \tag{5.11'}$$

$$|\Delta S_z| = \beta \frac{\gamma^2 B_1 B_2}{16} \frac{\omega_1}{\sqrt{(\omega_1-\omega_2)^2+T_1^{-2}}} \times \sum_{m=1}^{2I+1} \frac{1/T_2^m}{(\omega_1-\omega_0+m\omega_I)^2+(1/T_2^m)^2} . \tag{5.12'}$$

To derive the above equations, the small dynamical shift $\Delta\omega$ must be neglected with respect to T_2^{-1}. Equations (5.11') and (5.12') evidence that, if we sweep ω_1 and ω_2, their offset $|\omega_1-\omega_2|$ being constant, the LODESR signal $|\Delta S_z|$ reproduces the spectrum of Ψ_+ corresponding to the spectrum recorded in a usual electron spin resonance experiment [3,13,28,29].

The presence of secular terms in $H_{AB}(\mathbf{W})$ [Eq. (4.1b)], namely, terms commuting with S_z, causes T_2 to be shorter than T_1 when $\Delta^{-1} \gg \tau_c \gg \omega_0^{-1}$. In this region, if one sweeps the offset $|\omega_1-\omega_2|$ in a range larger than T_1^{-1} but smaller than T_2^{-1}, Eqs. (5.11') and (5.12') predict

$$|\Delta S_z| \cong \frac{K}{\sqrt{(\omega_1-\omega_2)^2+T_1^{-2}}} \propto |\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1-\omega_2)]| , \quad |\omega_1-\omega_2| \ll T_2^{-1} , \tag{5.13}$$

where K is a constant. Equation (5.13) shows that in the limit of fast fluctuation, more precisely if $\Delta^{-1} \gg \tau_c \gg \omega_0^{-1}$, the spectral profile reproduces the spectrum of $|\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1-\omega_2)]|$. This relationship is found for both two-level and multilevel systems. It is derived for a homogeneous line, but it is recovered also in the presence of inhomogeneous broadening mechanisms [29]. Numerical evidence of this effect will be given later.

Now, let us discuss the case of *slow* fluctuations, namely, $\Delta\tau_c \gg 1$. Because of Eq. (5.10) and neglecting off-resonance terms, Eq. (5.8) becomes

$$|\Delta S_z| = \beta \frac{\gamma^2 B_1 B_2}{16} \frac{1}{\sqrt{(\omega_1-\omega_2)^2+T_1^{-2}}} \times |\omega_1 \Psi_+(i\omega_1)+\omega_2 \Psi_-(-i\omega_2)| . \tag{5.14}$$

The breakdown of the time scale separation for the relaxation of the transverse part of the magnetization does not allow the writing down of $\Psi_\pm(i\omega)$ as a sum of Lorentzians. One must resort to the general approach of the generalized Langevin equations outlined in Sec. III C which express $\Psi_\pm(i\omega)$ as continued fractions of the kind given by Eq. (3.25).

From the structure of Eq. (3.25) it can be shown that, if $\omega_1 \approx \omega_2$, Eq. (5.14) reduces to

$$|\Delta S_z| = \beta \frac{\gamma^2 B_1 B_2}{8} \frac{\omega_1}{\sqrt{(\omega_1-\omega_2)^2+T_1^{-2}}} \mathrm{Re}\{\Psi_+(i\omega_1)\} . \tag{5.15}$$

The above relation tells us that also for slow fluctuations, if we sweep ω_1 and ω_2, their offset $|\omega_1-\omega_2|$ being constant, the LODESR signal $|\Delta S_z|$ reproduces the spectrum recorded in the usual electron spin resonance experiment [3,13].

One more interesting question about Eq. (5.14) is to check if one recovers the profile of $|\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1-\omega_2)]|$, by sweeping the offset $|\omega_1-\omega_2|$, also in the presence of slow fluctuations. A rough estimate provides the answer. For slow fluctuation $\Psi_+(i\omega)$ is expected to vary when ω is swept over a range comparable with Δ, the order of magnitude of the fluctuating fields. On the other hand, the region of interest of $|\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1-\omega_2)]|$ is swept if (4.26)

$$|\omega_1-\omega_2| \approx T_1^{-1} \cong \frac{\Delta^2}{\omega_0^2 \tau_c} \ll \Delta \tag{5.16}$$

since, due to Eqs. (4.3),

$$\omega_0 \tau_c \gg \Delta\tau_c \gg 1 . \tag{5.17}$$

So, once again, we expect also for slow fluctuations ($\Delta\tau_c \gg 1$) that

$$|\Delta S_z| \cong \frac{K}{\sqrt{(\omega_1-\omega_2)^2+T_1^{-2}}} = |\hat{\psi}_z^{\mathrm{CG}}[i(\omega_1-\omega_2)]| . \tag{5.18}$$

It will be shown later on that the further contribution to the linewidth given by the inhomogeneous broadening enhances this effect.

In the next section the general Hamiltonian [Eq. (4.1)] will be specialized to deal with two- and four-level systems affected by dichotomic noise. The model will be used to check the findings of this section.

A. Basic equations of the model

The model which will be outlined is the same model studied in I. It deals with a two-level system and a four-level system. The TLS is a particle with spin $S=\frac{1}{2}$. The FLS is a particle with spin $S=\frac{1}{2}$ interacting with a particle with spin $I=\frac{1}{2}$. The bath is pictured by introducing a scalar stochastic variable Ω, namely, $\mathbf{W} \equiv \Omega$. According to definitions given by Eq. (4.1) the spin Hamiltonian is separated as

$$H = H_A + H_{AB}(\Omega) , \tag{5.19}$$

where H_A is the part of the total Hamiltonian H independent of the stochastic process, which in turn affects $H_{AB}(\Omega)$. For a TLS

$$H_A = \omega_0 S_z , \tag{5.20a}$$

$$H_{AB}(\Omega) = \omega_z(\Omega) S_z + \omega_x(\Omega) S_x . \tag{5.20b}$$

$\omega_z(\Omega)$ and $\omega_x(\Omega)$ are scalar functions of the stochastic process Ω. The Hamiltonians of Eq. (5.20) drive a particle with spin $S=\frac{1}{2}$ which is put in a static magnetic field B_0 directed along the z axis. The particle precedes with Larmor frequency $\omega_0=\gamma_e B_0$ and is affected by a stochastic field with components $\omega_z(\Omega)$ and $\omega_x(\Omega)$ along the z and x axis, respectively. For a FLS

$$H_A=\omega_0 S_z+\omega_I S_z I_z \ , \tag{5.21a}$$

$$H_{AB}(\Omega)=\omega_x(\Omega)S_x+\omega_z(\Omega)S_z +\omega_{zx}(\Omega)S_z I_x+\omega_{xz}(\Omega)S_x I_z \ . \tag{5.21b}$$

$\omega_z(\Omega)$, $\omega_x(\Omega)$, $\omega_{zx}(\Omega)$, and $\omega_{xz}(\Omega)$ are scalar functions of the stochastic process Ω. Equations (5.21) differ from Eqs. (5.20) both in static and fluctuating terms which model the hyperfine interaction of the spin S with a second species with spin $I=\frac{1}{2}$ [13].

The structures of $H_{AB}(\Omega)$ of the TLS and the FLS include all the relevant kind of terms which are responsible for spin transitions, namely, *secular, nonsecular,* and *pseudosecular* terms. Secular terms flip neither spin S nor spin I, nonsecular terms flip spin S only, pseudosecular terms flip spin I only. The model Hamiltonian [Eq. (5.21)] is richer than the corresponding one of I, due to the nonsecular term $\omega_{xz}(\Omega)$.

We model the amplitudes $\omega_\alpha(\Omega)$ as

$$\omega_\alpha(\Omega)=\Omega\Delta_\alpha, \quad \alpha=z,x,zx,xz \ , \tag{5.22}$$

where Ω is a dichotomic, stationary Markov process (DMP) and Δ_α is the noise strength. With this choice, cross correlations occur between different $\omega_\alpha(\Omega)$. This effect is present in the notable case of motion of paramagnetic species in ordered fluids [28].

The DMP Ω has only two possible realizations, ± 1. The singlet distribution is expressed by the two-component vector $P(\Omega,t)=\{\frac{1}{2},\frac{1}{2}\}$ and the transition probability $T_\tau(\Omega|\Omega_0)\equiv T_\tau(\mathbf{W}|\mathbf{W}_0)$ obeys [Eq. (3.1)]

$$\frac{\partial}{\partial t}T_\tau(\Omega|\Omega_0)=\Gamma_\Omega T_\tau(\Omega|\Omega_0) \ , \tag{5.23}$$

where Γ_Ω is a 2×2 matrix

$$\Gamma_\Omega=\tfrac{1}{2}\gamma\begin{bmatrix}-1 & 1\\ 1 & -1\end{bmatrix} . \tag{5.24}$$

With the above choices Ω is with zero mean and exponential autocorrelation

$$\langle\Omega\rangle=0 \ , \qquad \langle\Omega(t)\Omega(t')\rangle=\exp(-\gamma|t-t'|) \ . \tag{5.25}$$

A useful result about DMP's is established by the following theorem [44]. If Ω is Markovian and if $\Psi[\Omega(\cdots)]$ is a functional involving only times prior to t_1 then for $t>t_1$

$$\langle\Omega(t)\Omega(t_1)\Psi[\Omega(\cdots)]\rangle=\langle\Omega(t)\Omega(t_1)\rangle\langle\Psi[\Omega(\cdots)]\rangle \ . \tag{5.26}$$

The observable of interest A evolves under the joint influence either of the spin Hamiltonians (5.20) or (5.21) affected by the DMP. The overall effect is accounted by the stochastic Liouville operator which introduces an effective *non-Hermitian* Liouvillian Γ_T of the form given by Eq. (3.12),

$$\Gamma_T=iH^\times+\Gamma_\Omega \ . \tag{5.27}$$

B. Results

In this section the nonlinear response and the relaxation behavior of the slow variables will be compared for the TLS and the FLS under the influence of dichotomic noise.

Let us introduce the parameter

$$R(\omega_1,\omega_1-\omega_2)=\left|\frac{\Delta S_z(\omega_1,\omega_1-\omega_2)}{\hat{\psi}_z[i(\omega_1-\omega_2)]}\right| . \tag{5.28}$$

By trivial manipulations $|\Delta S_z|$ can be recast in a form depending on ω_1 and the offset $\omega_1-\omega_2$. The parameter $R(\omega_1,\omega_1-\omega_2)$ evidences the discrepancies between the spectra of the LODESR spectroscopy and the relaxation of the longitudinal part of the electron magnetization. A weak dependence of R on the offset $\omega_1-\omega_2$ over a range larger than T_1^{-1} signals that the two spectra nearly coincide (apart from inessential constants).

In this section all the evaluations of $|\Delta S_z|$ *start from the general expression given by Eq. (5.2).* The expansion as continued fractions of the relevant matrix elements of the propagator G is derived by resorting to the generalized Langevin equation method (see Sec. III C). The method also provides the numerical expansion of $\hat{\psi}_z$. However, it must be noted that, if Eq. (4.3) holds, $\hat{\psi}_z$ is virtually given by the approximated form $\hat{\psi}_z^{CG}$ [Eqs. (4.7a) (4.28)] for both the TLS and the FLS (see I). Relevant to the present discussion are the expressions of the relaxation times T_1 and T_2 for the dichotomic relaxation model which, at second order in Δ, yields

$$\frac{1}{T_1}=\begin{cases}\dfrac{\Delta_x^2\gamma}{\omega_0^2+\gamma^2} & \text{(TLS)} \qquad (5.29)\\[2ex] \left(\dfrac{\Delta_x^2}{2}+\dfrac{\Delta_{xz}^2}{8}\right)\left(\dfrac{\gamma}{(\omega_0+\omega_I/2)^2+\gamma^2}+\dfrac{\gamma}{(\omega_0-\omega_I/2)^2+\gamma^2}\right) & \text{(FLS)} \ , \qquad (5.30)\end{cases}$$

and

$$\frac{1}{T_2}=\begin{cases}\dfrac{\Delta_z^2}{\gamma}+\dfrac{1}{2T_1} & \text{(TLS)}\\[2ex] \dfrac{\Delta_z^2}{\gamma}+\dfrac{\Delta_{zx}^2}{8}\dfrac{\gamma}{\omega_I^2/4+\gamma^2}+\dfrac{1}{2T_1} & \text{(FLS)} \ .\end{cases} \tag{5.31}$$

Let us analyze first the results for the TLS model.

The plot of $R(\omega_0,\omega_1-\omega_2)$ against $\omega_1-\omega_2$ is reported in Fig. 5 for different regimes of fluctuations. The convergence of $R(\omega_0,\omega_1-\omega_2)$ to a constant value $\bar{R}$ (by proper units $\bar{R}=1$) is expected for $\tau_c^{-1}=\gamma\ll\omega_0$. For the TLS the convergence is fast, being the unit value in practice reached for $\gamma<0.1\omega_0$. For fast fluctuations ($\gamma\geq\omega_0$)

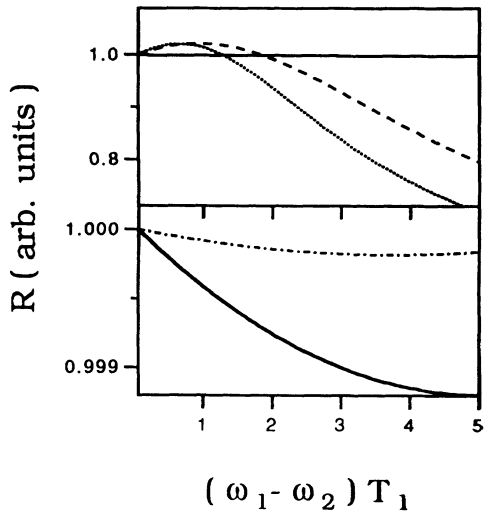

FIG. 5. TLS model. Plot of the ratio R against the offset $\omega_1-\omega_2$ for different fluctuation regimes. $\omega_0=1$, $\Delta_x=\Delta_z=0.1$. Continuous line, $\gamma=0.1$; dashed line, $\gamma=0.7$; dotted line, $\gamma=1$; dot-dashed line, $\gamma=0.01$.

$R(\omega_0,\omega_1-\omega_2)$ departs from the unit value because $T_1=T_2$ and Eq. (5.11) cannot be approximated by Eq. (5.13) on a range of values $|\omega_1-\omega_2|$ comparable with T_1. For slower fluctuations ($\gamma<\omega_0$) T_1 fairly exceeds T_2 and $R(\omega_0,\omega_1-\omega_2)$ tends to one. For even slower fluctuations ($\gamma>\Delta$) T_2 cannot be defined. Nonetheless the convergence of $R(\omega_0,\omega_1-\omega_2)$ to one goes on.

In Fig. 6 the convergence is studied for different amplitudes of the fluctuating fields. Note that the fluctuation rate γ is fast. For slower rates $R(\omega_0,\omega_1-\omega_2)$ would be much closer to the unit value, according to Fig. 5. The trends of Fig. 6 are easily understood, if one recalls that

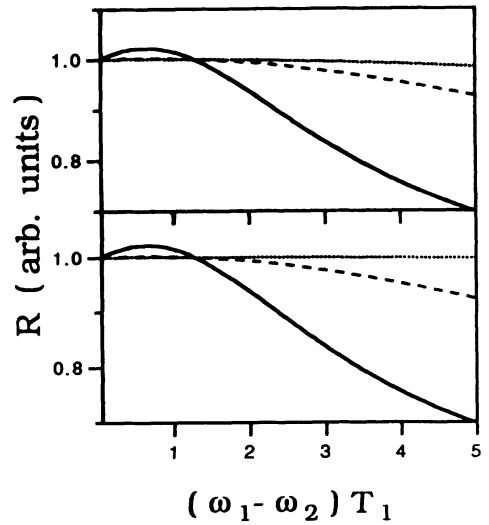

FIG. 6. TLS model. Plot of the ratio R against the offset $\omega_1-\omega_2$ for different amplitudes of the fluctuating fields. $\omega_0=1$, $\gamma=1$. Upper part: $\Delta_x=0.1$; continuous line, $\Delta_z=0.1$; dashed line, $\Delta z=0.2$; dotted line, $\Delta_z=0.3$. Lower part: $\Delta_z=0.1$; continuous line, $\Delta_x=0.1$; dashed line, $\Delta_x=0.05$; dotted line, $\Delta_x=0.02$.

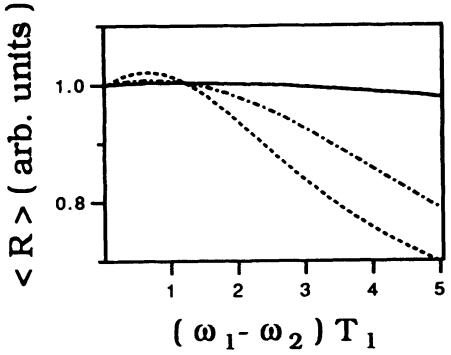

FIG. 7. TLS model. Plot of the ratio $\bar{R}$ against the offset $\omega_1-\omega_2$ in the presence of inhomogeneous broadening. $\bar{\omega}_0=1$, $\gamma=1$, $\Delta_x=\Delta_z=0.1$. Dashed line, $\Delta\omega_0=0$; dot-dashed line, $\Delta\omega_0=0.01$; continuous line, $\Delta\omega_0=0.1$.

$R(\omega_0,\omega_1-\omega_2)$ is closer to the unit value if either the secular terms are more effective, the nonsecular terms are less effective, or both the above conditions are fulfilled.

In Fig. 7 the effect of the inhomogeneous broadening is presented. Inhomogeneous broadening can be introduced by distributing the Larmor frequencies ω_0 [13]. The ratio R defined by Eq. (5.28) is evaluated by replacing ΔS_z with its value averaged on the distribution of ω_0, ΔS_z. Figure 7 presents the results for a Gaussian distribution with a width $\Delta\omega_0$ centered at $\bar{\omega}_0$. It points out that the inhomogeneous broadening improves the agreement between $\overline{\Delta S_z}$ and $\hat{\psi}_z$.

Figure 8 presents the effects arising in the region $\Delta\approx\omega_0$ where Eq. (4.3) breaks down. In this region the

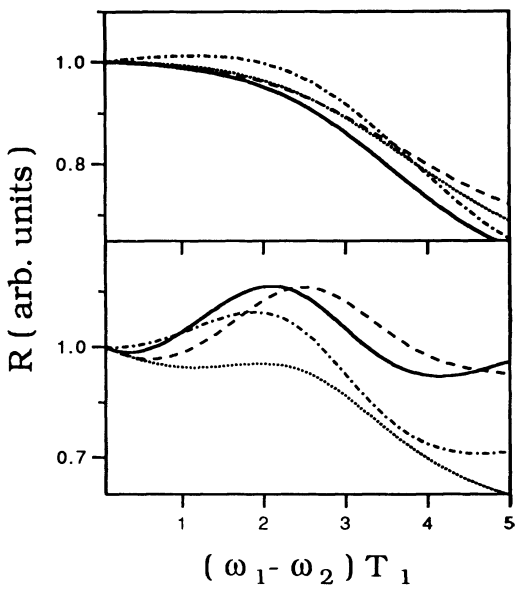

FIG. 8. TLS model. Plot of the ratio $\bar{R}$ against the offset $\omega_1-\omega_2$ for different approximated expansions of the first vertex. $\omega_0=1$, $\gamma=1$. Upper part: $\Delta_x=\Delta_z=0.6$. Lower part: $\Delta_x=\Delta_z=0.8$. Continuous line: exact expansion; dashed line: excited bath state neglected; dot-dashed line: spin state $S_\pm$ neglected; dotted line: only S_z and equilibrium bath state included.

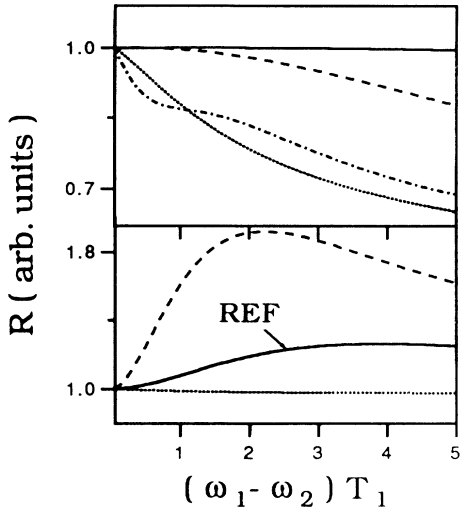

FIG. 9. FLS model. Plot of the ratio R against the offset $\omega_1-\omega_2$ for different fluctuation regimes. The curve indicated as "REF" is a reference curve to facilitate the comparison with the curves plotted in Fig. 10. $\omega_0=1$, $\Delta_x=\Delta_{zx}=\Delta_{xz}=\Delta_z=0.1$. Upper part: $\omega_I=0.01$; continuous line: $\gamma=0.1$; dashed line, $\gamma=0.2$; dot-dashed line, $\gamma=0.4$; dotted line, $\gamma=0.5$. Lower part: $\omega_I=0.1$; dashed line, $\gamma=1$; continuous line (REF curve), $\gamma=0.4$; dotted line, $\gamma=0.2$.

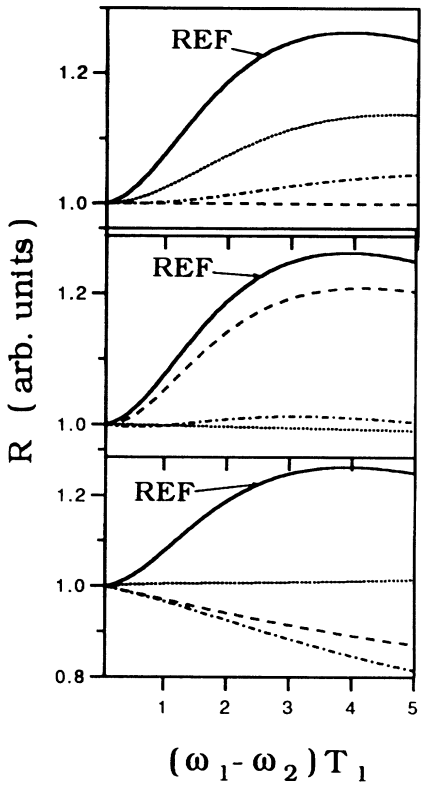

FIG. 10. FLS model. Plot of the ratio R against the offset $\omega_1-\omega_2$ for different amplitudes of the fluctuating fields. $\omega_0=1$, $\omega_I=0.1$, $\gamma=0.4$. Top: changing nonsecular terms, $\Delta_{zx}=\Delta_z=0.1$; continuous line, $\Delta_x=\Delta_{xz}=0.1$; dotted line, $\Delta_x=\Delta_{xz}=0.08$; dot-dashed line, $\Delta_x=\Delta_{xz}=0.06$; dashed line, $\Delta_x=\Delta_{xz}=0.01$. Middle: changing secular term, $\Delta_x=\Delta_{xz}=\Delta_{zx}=0.1$; continuous line, $\Delta_z=0.1$; dashed line, $\Delta_z=0.12$; dot-dashed, $\Delta_z=0.2$; dotted line, $\Delta_z=0.3$. Bottom: changing pseudosecular term, $\Delta_x=\Delta_{xz}=\Delta_z=0.1$; continuous line, $\Delta_{zx}=0.1$; dashed line, $\Delta_{zx}=0.2$; dot-dashed line, $\Delta_{zx}=0.3$; dotted line, $\Delta_{zx}=0.8$.

atom state S_z is not slow. To better understand Fig. 8 one must recall that ΔS_z is evaluated via Eq. (5.2) by resorting to the general expression Eq. (3.18b). During the propagation, due to the decreased time scale separation at the first atom-radiation interaction (i.e., at the first vertex labeled by 1) the bath cannot be considered in equilibrium. Technically, this implies that in the *correct* vertex expansion, besides the bath equilibrium state $|b_0\rangle$, also the excited bath states, namely, states $|b_{i_1}\rangle$ with $i_1>0$ must be included. Furthermore, the reduced time scale separation mixes up the time evolution of the three components of the spin and this implies that the vertex expansion must also include all the three components of the spin and not only S_z. The curves show that if $\Delta\approx\omega_0$ the excited bath states and spin states other than S_z play relevant roles in the definition of the spectrum of ΔS_z. This effect explodes if Δ is closer and closer to ω_0. Moreover, in the region $\Delta\approx\omega_0$ R is fairly different from the unit value.

Figures 9–11 show the results for $R(\omega_0+\omega_I/2, \omega_1-\omega_2)$ by referring to the FLS model. No remarkable differences between the TLS and FLS cases are observed. Figure 9 exhibits the dependence of R on the offset $\omega_1-\omega_2$ for several fluctuation regimes and different values of the hyperfine splitting ω_i. The curve marked as "REF" is a reference curve to compare Fig. 9 with Fig. 10 where the dependence of R on the amplitudes of the fluctuating fields is studied. Finally, Fig. 11 shows the effect of inhomogeneous broadening included in the calculations, as for the TLS.

The results presented in Figs. 6–8, 10, and 11 shed light on the deviation from the unit value of the ratio R when $\gamma\approx\omega_0$. It must be stressed that, if $\gamma,\Delta<0.1\omega_0$, this

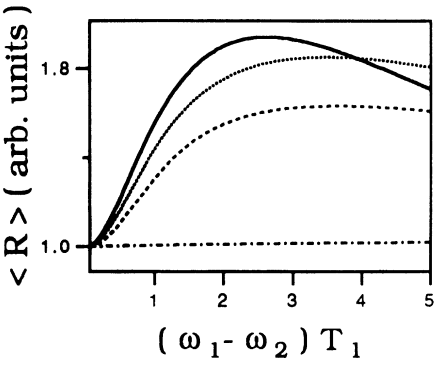

FIG. 11. FLS model. Plot of the ratio $\bar{R}$ against the offset $\omega_1-\omega_2$ in the presence of inhomogeneous broadening, $\omega_0=1$, $\omega_I=0.1$, $\Delta_x=\Delta_{zx}=\Delta_{xz}=\Delta_z=0.1$, $\gamma=1$. Continuous line, $\Delta\omega_0=0.01$; dotted line, $\Delta\omega_0=0.03$; dashed line, $\Delta\omega_0=0.04$; dot-dashed line, $\Delta\omega_0=0.05$.

deviation becomes negligible for any practical purposes (see Figs. 5 and 9).

VI. CONCLUSIONS

The present paper has investigated the relationship between the nonlinear response of a system of interest, the atom system, subjected to external disturbances and the relaxation effects caused by a thermal bath. This topic has attracted great interest in the recent past and substantial work was done by Kubo and collaborators [2,19–25], Louisell [35], Van Kampen [37], and Risken [38]. The point of view of the master equation and its generalized forms [45] has been developed by Agarwal [46], Montroll and West [47], and Zwanzig [48], whereas applications to problems in nonlinear response and optics are discussed in great detail by Haken [49].

A general quantal scheme has been proposed to extend the classical results of the linear-response theory in order to discuss the relationship between the *nonlinear* response and the relaxation induced by colored noise. The scheme takes into account in a systematic way the higher-order contributions to the susceptibility with respect to the amplitude of the external fields. It has been proven that each contribution referring to a definite order of perturbation can be factorized in two terms, namely, the radiation term including solely the degrees of freedom of the external fields and the atom-bath term including solely the degrees of freedom of the atom and the bath.

Closer resemblance with the results of linear-response theory comes into view by selecting properly "slow" atom states whose relaxation time T is longer than the microscopic correlation time τ_c. The relaxation behavior of slow atom states has been thoroughly examined in a previous paper [31]. A general discussion on the methods of separation of coupled systems with widely differing relaxation time scales is provided by Haken [49]. Show atom states play a fundamental role in order to relate the nonlinear response to *equilibrium* correlation functions. We have derived expressions for the second- and third-order susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$, respectively, in the framework of a general stochastic scheme. $\chi^{(2)}$ and $\chi^{(3)}$ have been related to the response and relaxation functions Φ and Ψ, respectively.

This paper has examined the character of the nonlinear response for a fairly general model of the atom system in magnetic resonance experiments. In this framework we have identified a regime characterized by slow fluctuations ($\gamma < \omega_0$) with small amplitudes ($\Delta < \omega_0$) where nonlinear spectroscopies of proper design exhibit line shape proportional to the spectrum of the slow atom state. Comparing the predictions of the theory with previous experimental work (see Ref. [29], and references quoted therein) has clarified the degree of meaningfulness of previous Bloch-like treatments.

The findings of the present paper claim that measuring nonlinear susceptibilities provides competitive and *viable* routes to pulsed methods to measure relaxation phenomena even in cases where practical studies put extreme demands on technical conditions.

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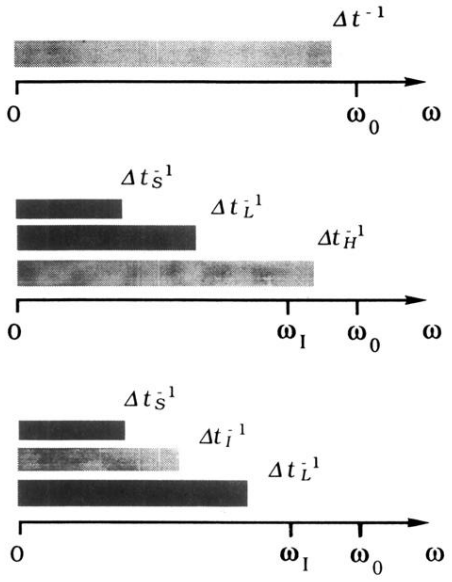

FIG. 3. Mutual positions of the resonances of the atom, the bandwidth $1/\Delta t$ covered by the coarse-grained procedure, and the rates of the atom relaxation processes. ω_0 is the Zeeman splitting, ω_I is the hyperfine splitting of the $2I+1$ levels forming each multiplet. Δt_s^{-1}, Δt_I^{-1} are the order of magnitude of the intermultiplet and intramultiplet relaxation rates, respectively. Δt is the time interval on which coarse graining is carried out. Top: TLS case. Middle: FLS case, high accuracy $\Delta t_H^{-1} > \omega_I$ vs low accuracy $\Delta t_L^{-1} < \omega_I$. Bottom: FLS case, improved low accuracy $\Delta t_L^{-1} > \Delta t_I^{-1}$. See text for details.