

Dynamics of Stochastic Systems: Effect on Spectral Line Shapes

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Abstract

We present a theoretical approach to describe the dynamics of a system induced by stochastic couplings and undergoing dephasing processes. We consider a model frequently encountered in the study of non-radiative transitions in molecular systems, the case of two configurations stochastically coupled. In this model, we use a system whose excited radiant state is coupled stochastically to a non-radiant state of a lower electronic configuration. We show the line shape for stochastic non-diagonal perturbations to remain Lorentzian. This result is different from the case of frequency modulation where a transition from a Gaussian to a Lorentzian line shape can be observed.

Key Words: Non-radiative transition, stochastic approach, relaxation and dephasing processes, absorption spectrum.

1. Introduction

The problem of spectral line shapes has gained considerable interest in recent decades. In fact, it has been recognized that physical observations cannot be fully understood without a clear picture of the quantum-mechanical source of fluctuations and dissipation caused by the interaction of the system with the surrounding heat bath. Well-know model treatments in the field of spectroscopy are the line shape theories due to Anderson [1], Kubo and Tomita [2], in which the bath degrees of freedom are assumed to give rise to white noise or Markovian limit, in which the correlation function is represented by Dirac delta function δ . In this case, the relaxation behavior of a molecular system can then be described by Bloch optical equations [3, 4] including two phenomenological decay parameters (T_1^{-1} and T_2^{-1} representing longitudinal and transverse relaxation, respectively). The corresponding treatment for the coupled coherent and incoherent motion of a quantum particle in fluctuating medium is due to Haken, Strobl, and Reineker [5–7]. Here, stochasticity has been introduced to describe the behavior of excitons in the molecular aggregates, and in which the exciton-phonon coupling is treated phenomenologically and semiclassically via the introduction of a stochastic term in the Hamiltonian. For colored noise, i.e., a non-Markovian stochastic process with exponentially decaying correlation functions, the spectroscopic line shape aspect is due to Faïd and Fox [8–10] who treated the deviation from the situation as a perturbation. However, it is remarkable that stochasticity plays an important role, in particular, in the internal dynamics of the molecules. Works [11–16] on the study of the

non-radiative transitions in molecular compounds show that these transitions affect the dynamics of the system. These works were devoted to the evaluation of non-radiative decay rates associated with electronic or vibrational relaxation processes. The studies varied from the energy dependence of electronic relaxation processes [11, 12], to the search for criteria irreversible electronic transitions [13–15], to the dependence of these criteria on the nature of the non-radiative processes, to the real nature of the molecular eigenstate [16]. That said, the interaction responsible for the non-radiative transitions has been considered as a purely quantum interaction which depends on the particular process of interest, such as internal conversion, intersystem crossing, etc. From these observations, a stochastic approach offers an interesting alternative to the description of these processes. More recently, stochasticity has also appeared in the intermediate state during a resonant optical process of the second order [17–19]. The case of organic dye molecules in solution is of particular interest since the Raman signals are strong while the fluorescence is weak. As such, the interaction with surrounding solvent molecules can suitably modulate the energy of the intermediate state. Note that an interesting consequence of the statistical distribution of the stochastic interactions is a decoupling of the dynamical equations of the averaged density matrix elements as opposed to the microscopic quantum case. Indeed, study of the internal dynamics of a system induced by stochastic couplings and undergoing dephasing processes has been treated in a Doctoral thesis [20] and in papers [21, 22]. The focus concerned the relation between frequency modulation and diagonal stochastic perturbations [23–25], recent developments in the more general case of the non-diagonal stochastic interaction [8–10] leading to a generalization of the stochastic theory of line shape, and relaxation of Kubo [24]. The principal result is the appearance of a profile of line shape asymmetry which gives a measure of the degree of anisotropy of the stochastic interaction [8].

In this work, we present an application relevant to stochastic approach to non-radiative transitions. We assume that the stochastic interaction are applied only to excited states, whereas the relaxation of the system is ensured by a purely quantum heat bath. By taking advantage of the stochastic theory presented in [8], we develop in Section II a general theory of the stochastic to describe the dynamics induced by the stochastic interactions for a system undergoing relaxation and dephasing processes as well as pure dephasing processes. In Section III, we consider a particular model frequently encountered in the study of non-radiative transitions in molecular systems. We restrict our model a stochastic interaction to couple the radiant state to the non-radiant state. Finally, in Section IV, a detailed analysis of the absorption spectra is given.

2. Theoretical Considerations

In this section, we develop a theory to describe the internal dynamics of stochastic systems. Only the dynamical evolution of the free system is accounted for here, the interacting fields being introduced as a usual perturbation calculation up to a given order, depending on the nature of the physical process. This formalism has advantage over previous theoretical approaches in that it describes the evolution of stochastic systems undergoing relaxation and dephasing processes, including pure dephasing [26, 27]. In fact, the descriptions developed in the literature requiring spectral decomposition methods are inappropriate to account for pure dephasing. Also, this approach is not restricted to the usual single-line approximation, which breaks down when the resonance overlapping cannot be neglected [28, 29].

We consider a system coupled to a heat bath and undergoing stochastic perturbation. The total Hamiltonian can be written as

$$H = H_s + H_b + \tilde{H} + H_{sb} = H_0 + \tilde{H} + H_{sb}, \quad (2.1)$$

where H_s and H_b refer to the Hamiltonian for the system and H_{sb} represents the interaction between the system and the heat bath. The system in addition is stochastically perturbed by the interaction $\tilde{H}(t)$. The

Liouville equation describing the motion of density matrix $\rho(t)$ is

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [H_0 + \tilde{H}(t) + H_{sb}, \rho(t)] \equiv -\frac{i}{\hbar} [L_0 + \tilde{L}(t) + L_{sb}] \rho(t), \quad (2.2)$$

where

$$L_0 \equiv [H_s + H_b], \quad (2.3)$$

$$\tilde{L}(t) \equiv [\tilde{H}(t)], \quad (2.4)$$

and

$$L_{sb} \equiv [H_{sb}], \quad (2.5)$$

represent the Liouville operators corresponding to H_0 , \tilde{H} and H_{sb} , respectively. Notice that the commutator operator $[A, B] = AB - BA$. The formal solution takes the form

$$\rho(t) = \exp \left[-\frac{i}{\hbar} L_0 t \right] \bar{T} \exp \left\{ -\frac{i}{\hbar} \int_0^t d\tau [\tilde{L}_I(\tau) + L_{sbI}(\tau)] \right\} \rho(0), \quad (2.6)$$

where \bar{T} denotes the time-ordering operator and $\rho(0)$ represents the density matrix at the initial time $t = 0$. In addition, $\tilde{L}_I(t)$ is the Liouville operator in the interaction representation

$$\tilde{L}_I(t) = \exp \left[\frac{i}{\hbar} L_0 t \right] \tilde{L}(t) \exp \left[-\frac{i}{\hbar} L_0 t \right]. \quad (2.7)$$

Using the cumulant expansion method [23, 30], and developing the expression of the average density matrix for the material system alone up to the second order, we obtain

$$\langle \rho^s(t) \rangle = \exp \left[-\frac{i}{\hbar} L_0 t \right] \bar{T} \exp \left\{ -\frac{i}{\hbar} \int_0^t d\tau \int_0^\tau d\lambda [\langle \tilde{L}_I(\tau) \tilde{L}_I(\lambda) \rangle + \langle L_{sbI}(\tau) L_{sbI}(\lambda) \rangle] \right\} \langle \rho^s(0) \rangle, \quad (2.8)$$

where the notation

$$L_{sbI}(t) = \exp \left[\frac{i}{\hbar} (L_s + L_b) t \right] L_{sb} \exp \left[-\frac{i}{\hbar} (L_s + L_b) t \right] \quad (2.9)$$

has been introduced. It will be noted that the average of the first term in the expression (2.8) is over the stochastic variables while the one of the second term is over the bath states. The first order cumulants are assumed to be zero.

$$\langle \tilde{L}_I(\tau) \rangle = 0 \quad (2.10)$$

$$Tr_b [L_{sbI}(\tau) \rho^b(0)] = 0,$$

without loss of generality. Then, the general equation of motion of the material system is given by

$$\frac{\partial \langle \rho^s(t) \rangle}{\partial t} = -\frac{i}{\hbar} [L_s + R(t)] \langle \rho^s(t) \rangle, \quad (2.11)$$

where

$$R(t) = -i\hbar [\Gamma_S(t) + \Gamma(t)], \quad (2.12)$$

the stochastic operator $\Gamma_S(t)$ is defined by

$$\Gamma_S(t) = \frac{1}{\hbar^2} \int_0^t d\tau \left\langle \tilde{L}(t) \exp \left[-\frac{i}{\hbar} (t - \tau) L_s \right] \tilde{L}(\tau) \exp \left[\frac{i}{\hbar} (t - \tau) L_s \right] \right\rangle \quad (2.13)$$

and the usual damping operator $\Gamma(t)$ by

$$\Gamma(t) = \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_b \left\{ L_{sb} \exp \left[-\frac{i}{\hbar} (t - \tau) (L_s + L_b) \right] L_{sb} \exp \left[\frac{i}{\hbar} (t - \tau) (L_s + L_b) \right] \rho^b(0) \right\}, \quad (2.14)$$

where $\rho^b(0)$ represents for initial density matrix of the bath. In the following, the bath generating the constant $\Gamma(t)$ is assumed to be purely Markovian. Its matrix elements are related the total decay rate Γ_{nnnn} of the state n , the transition rate Γ_{nnmm} from state m to state n and dephasing constants Γ_{nmnm} related to states n and m , and is given by [26]

$$\Gamma_{nmnm} = \frac{1}{2} [\Gamma_{nnnn} + \Gamma_{mmmm}] + \Gamma_{nm}^{(d)}, \quad (2.15)$$

where $\Gamma_{nm}^{(d)}$ denotes the pure dephasing constant originating from the elastic interaction process molecules and heat bath. Throughout this work, the damping operator will insure the thermalization of the material system. We still mention that an explicit form of the matrix elements of the tetradic $\Gamma_S(t)$ can be evaluated in the molecular model in the following section.

3. The Molecular Model and Calculation Procedure

In this section, we consider the Feed-Jortner model [31], which has played a central role as a prototype in the study of non-radiative decay in organic compounds. This model is based on a quantum interaction which depends on the nature of non-radiative transitions, such as internal conversion, intersystem crossing, etc. Stochastic approaches offer an interesting alternative to the description of these processes. In addition, the simplification resulting from the statistical distribution enables the introduction of the dephasing processes. Also, for the sake of convenience, we introduce the stochasticity in terms of the correlation function of the interaction [9]

$$\langle \tilde{H}_{ij}(t) \tilde{H}_{kl}(\tau) \rangle = \hbar^2 \frac{(\delta\omega_{ijkl})^2}{2} \exp[-\varepsilon_{ijkl} |t - \tau|], \quad (3.1)$$

where the constant $\delta\omega$, defined by

$$\delta\omega_{ijkl} = \delta\omega_{ijji} \delta_{il} \delta_{jk}, \quad (3.2)$$

denotes the amplitude of the fluctuations and ε^{-1} in their time scale (correlation time). This has the advantage over the previous definitions of keeping the various stochastic variables completely independent so that diagonal as well as non-diagonal stochastic coupling can be treated simultaneously of the same footing. Also, we observe the same decoupling in the equation of motion of the populations and coherences. We still need the explicit expressions of the stochastic operator $\Gamma_S(t)$ which drives the evolution of the average density matrix of the material system alone. It takes the form

$$\begin{aligned} [\Gamma_S(t) \langle \rho(t) \rangle]_{ij} &= \frac{1}{2} \sum_p \left\{ (\delta\omega_{ippi})^2 \frac{1 - \exp[-(\varepsilon_{ippi} + i\omega_{pi})t]}{\varepsilon_{ippi} + i\omega_{pi}} \langle \rho_{ij}(t) \rangle \right. \\ &\quad \left. - (\delta\omega_{piip})^2 \delta_{ij} \frac{1 - \exp[-(\varepsilon_{piip} + i\omega_{ip})t]}{\varepsilon_{piip} + i\omega_{ip}} \langle \rho_{pp}(t) \rangle \right\} \end{aligned}$$

$$\begin{aligned}
 & - (\delta\omega_{ippi})^2 \delta_{ij} \frac{1 - \exp[-(\varepsilon_{ippi} + i\omega_{pi})t]}{\varepsilon_{ippi} + i\omega_{pi}} \langle \rho_{pp}(t) \rangle \\
 & + (\delta\omega_{pjpp})^2 \frac{1 - \exp[-(\varepsilon_{pjpp} + i\omega_{jp})t]}{\varepsilon_{pjpp} + i\omega_{jp}} \langle \rho_{ij}(t) \rangle \}.
 \end{aligned} \tag{3.3}$$

From the identification of this expression with the formal development

$$[\Gamma_S(t) \langle \rho(t) \rangle]_{ij} = \sum_{i,j} \Gamma_{S \quad ij \quad pq}(t) \langle \rho_{pq}(t) \rangle, \tag{3.4}$$

and after some simplifications, the matrix elements of the stochastic operators can be expressed as

$$\Gamma_{Sijpq}(t) = \Gamma_{Sijpq}^{(1)}(t) + \Gamma_{Sijpq}^{(2)}(t), \tag{3.5}$$

where

$$\Gamma_{Sijpq}^{(1)}(t) = \frac{1}{2} \sum_l \left\{ (\delta\omega_{illi})^2 \frac{1 - \exp[-(\varepsilon_{illi} + i\omega_{li})t]}{\varepsilon_{illi} + i\omega_{li}} + (\delta\omega_{ljjl})^2 \frac{1 - \exp[-(\varepsilon_{ljjl} + i\omega_{jl})t]}{\varepsilon_{ljjl} + i\omega_{jl}} \right\} \delta_{ip} \delta_{jq} \tag{3.6}$$

$$\Gamma_{Sijpq}^{(2)}(t) = -\frac{1}{2} \left\{ (\delta\omega_{piip})^2 \frac{1 - \exp[-(\varepsilon_{piip} + i\omega_{ip})t]}{\varepsilon_{piip} + i\omega_{ip}} + (\delta\omega_{ippi})^2 \frac{1 - \exp[-(\varepsilon_{ippi} + i\omega_{pi})t]}{\varepsilon_{ippi} + i\omega_{pi}} \right\} \delta_{ij} \delta_{pq} \tag{3.7}$$

In what follows, we apply this approach to a material system where the essential part of the internal dynamics can be described by a radiant excited state coupled via a stochastic perturbation. In Figure 1 is show one non-radiant state of a lower electronic configuration.

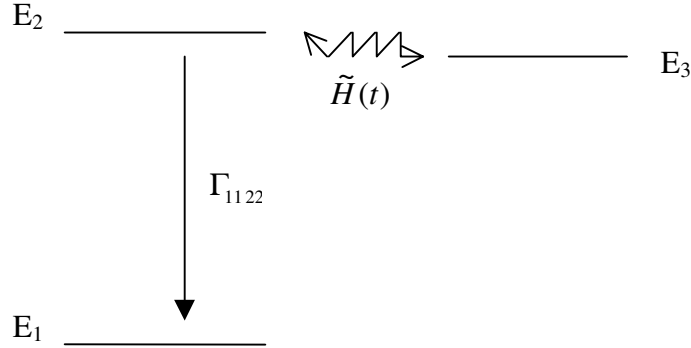


Figure 1. Energy-level scheme of the material system used to study the effect of non-diagonal perturbations between states $|2\rangle$ and $|3\rangle$ on the absorption spectra.

The coupling between the radiant state and non-radiant is induced by the non-diagonal stochastic perturbation $\tilde{H}(t)$, where the average is supposed to be zero and a correlation function in second-order is given by

$$\langle \tilde{H}_{23}(t) H_{32}(t) \rangle = \hbar^2 \frac{(\delta\omega_{3223})^2}{2} \exp(-\varepsilon_{3223} |t - \tau|). \tag{3.8}$$

In this approach, we calculated the populations and the coherence for the evaluation the optical line shapes. For this purpose, we introduce the Liouville equation of the total density matrix $\rho(t)$:

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [L_0 + R(t) + L_{V_0}] \rho(t). \tag{3.9}$$

Here, L_0 represents the sum of Liouvillians of the free system L_s , the radiation field L_f is defined by

$$L_f = [\hbar\omega_0 C_0^+ C_0], \quad (3.10)$$

and the Liouvillian L_{V_0} associated with the field- system interaction is given by

$$L_{V_0} = [V_{12} |1\rangle \langle 2| C_0^+ + V_{21} C_0 |2\rangle \langle 1|], \quad (3.11)$$

In the previous expressions, C_0 and C_0^+ denotes the annihilation and creation operators, respectively, of a photon of frequency ω_0 associated with the radiation field. In addition the operators of the Liouville $R(t)$ previously described, includes the non-Markovian case of the stochastic operator $\Gamma_S(t)$, and the usual damping operator Γ describes spontaneous emission. For our model the matrix elements of the $R(t)$ are assumed to be zero: $R_{2211}(t) = R_{3311}(t) = 0$.

The equation of motion of the matrix elements density can be written

$$\frac{\partial \rho_{22}(t)}{\partial t} = -\frac{i}{\hbar} [R_{2222}(t)\rho_{22}(t) + R_{2233}(t)\rho_{33}(t) + V_{021}\rho_{12}(t) - V_{012}\rho_{21}(t)]$$

$$\frac{\partial \rho_{33}(t)}{\partial t} = -\frac{i}{\hbar} [R_{3322}(t)\rho_{22}(t) + R_{3333}(t)\rho_{33}(t)]$$

$$\frac{\partial \rho_{12}(t)}{\partial t} = -\frac{i}{\hbar} [(R_{1212}(t) + E_{12})\rho_{12}(t) + V_{012}(-1 + 2\rho_{22}(t) + \rho_{33}(t))], \quad (3.12a)$$

$$\frac{\partial \rho_{13}(t)}{\partial t} = -\frac{i}{\hbar} [(R_{1313}(t) + E_{13})\rho_{13}(t) + V_{12}\rho_{23}(t)]$$

$$\frac{\partial \rho_{23}(t)}{\partial t} = -\frac{i}{\hbar} [(R_{1313}(t) + E_{23})\rho_{23}(t) + V_{21}\rho_{13}(t)], \quad (3.12b)$$

to which should be added the well known relations of conservation of the populations and complex conjugation of the coherences $\rho_{mn}(t)$. We will note in relations (3.12) the decoupling between the populations $\rho_{22}(t)$ and $\rho_{33}(t)$, and coherence $\rho_{12}(t)$ on the one hand, and the coherences $\rho_{13}(t)$ and $\rho_{23}(t)$ on the other hand. We start by solving the second equations of system (3.12). If we consider the solution in the zero order approximation, this equation becomes

$$\frac{\partial \rho_{23}^{(0)}(t)}{\partial t} = -\frac{i}{\hbar} [R_{2323}(t) + E_{23}]\rho_{23}^{(0)}(t) \quad (3.13)$$

which, taking into account the initial conditions $\rho_{13}^{(0)}(0) = \rho_{23}^{(0)}(0) = 0$, give

$$\rho_{13}^{(0)}(t) = \rho_{23}^{(0)}(t) = 0. \quad (3.14)$$

Next, we consider the first order approximation, the equations take the form

$$\frac{\partial \rho_{13}^{(1)}(t)}{\partial t} = -\frac{i}{\hbar} [(R_{1313}(t) + E_{13})\rho_{13}^{(1)}(t) + V_{012}\rho_{23}^{(0)}(t)]$$

$$\frac{\partial \rho_{23}^{(1)}(t)}{\partial t} = -\frac{i}{\hbar} [(R_{2323}(t) + E_{23})\rho_{23}^{(1)}(t) + V_{021}\rho_{13}^{(0)}(t)] \quad (3.15)$$

and using relation (3.15) we obtain the same solutions previously determined

$$\rho_{13}^{(1)}(t) = \rho_{23}^{(1)}(t) = 0. \quad (3.16)$$

Similarly, by recurrence, for order n , we have $\rho_{13}^{(n)}(t) = \rho_{23}^{(n)}(t) = 0$. Consequently, the coherences $\rho_{13}(t)$ and $\rho_{23}(t)$ are rigorously zero for this system. We also have to determine the populations and coherence $\rho_{12}(t)$. Here, we still have to solve the equation of system from the perturbation method. We find for the zero order approximation

$$\begin{aligned} \frac{\partial \rho_{22}^{(0)}(t)}{\partial t} &= -\frac{i}{\hbar} \left[R_{2222}(t) \rho_{22}^{(0)}(t) + R_{2233}(t) \rho_{33}^{(0)}(t) \right] \\ \frac{\partial \rho_{33}^{(0)}(t)}{\partial t} &= -\frac{i}{\hbar} \left[R_{3322}(t) \rho_{22}^{(0)}(t) + R_{3333}(t) \rho_{33}^{(0)}(t) \right] \\ \frac{\partial \rho_{12}^{(0)}(t)}{\partial t} &= -\frac{i}{\hbar} \left[R_{1212}(t) + E_{12} \right] \rho_{12}^{(0)}(t). \end{aligned} \quad (3.17)$$

If we assume at initial time the material system in the ground state $|1\rangle$, then the solutions for the zero order can be simplified to

$$\rho_{22}^{(0)}(t) = \rho_{33}^{(0)}(t) = \rho_{12}^{(0)}(t) = 0. \quad (3.18)$$

Similarly, for the first order, the system of equations become

$$\begin{aligned} \frac{\partial \rho_{22}^{(1)}(t)}{\partial t} &= -\frac{i}{\hbar} \left[R_{2222}(t) \rho_{22}^{(1)}(t) + R_{2233}(t) \rho_{33}^{(1)}(t) + V_{021} \rho_{12}^{(0)}(t) - V_{012} \rho_{21}^{(0)}(t) \right] \\ \frac{\partial \rho_{33}^{(1)}(t)}{\partial t} &= -\frac{i}{\hbar} \left[R_{3322}(t) \rho_{22}^{(1)}(t) + R_{3333}(t) \rho_{33}^{(1)}(t) \right] \\ \frac{\partial \rho_{12}^{(1)}(t)}{\partial t} &= -\frac{i}{\hbar} \left[(R_{1212}(t) + E_{12}) \rho_{12}^{(1)}(t) + V_{012} \left(-1 + 2\rho_{22}^{(0)}(t) + \rho_{33}^{(0)}(t) \right) \right]. \end{aligned} \quad (3.19)$$

The first order corrections to populations are zero:

$$\rho_{22}^{(1)}(t) = \rho_{33}^{(1)}(t) = 0. \quad (3.20)$$

Then, the contribution to coherences is nonzero, and the formal solution takes the form

$$\rho_{12}^{(1)}(t) = \frac{i}{\hbar} \int_0^t d\tau V_{012} \exp \left[-\frac{i}{\hbar} \int_{t_1}^t d\tau (R_{1212}(\tau) + E_{12}) \right]. \quad (3.21)$$

Therefore, we are now able to determine the absorption spectrum. At this stage, it is essential to note that contrary to the case frequency modulation, here E_{12} include the energy zero order of the material system and of the field given by energy $\hbar\omega_0$. Under these conditions, $E_{12} = E_1 - E_2 + \hbar\omega_0$.

4. Absorption Spectrum

In this section, we shall apply the theoretical results developed in the previous sections to the absorption spectrum. The expression of the absorption spectrum results from the decrease of the incident beam intensity

as a function of the frequency. Consequently, the absorption spectrum is deduced from the radiation field, and its observable can be defined by

$$S(\omega_0, t) = -\frac{d}{dt}C_0^+C_0. \quad (4.1)$$

This observable can be still written under the terms of the Heisenberg equation of motion for the operators,

$$\begin{aligned} S(\omega_0, t) &= -\frac{i}{\hbar} [H(t), C_0^+C_0] \\ &= -\frac{i}{\hbar} [V_0, C_0^+C_0], \end{aligned} \quad (4.2)$$

since all the parts the Hamiltonian of the total system commute with $C_0^+C_0$. The absorption spectrum is now given by the averaged of this observable evaluated at first order one of this operator, that is to say

$$I_{Ab}(\omega_0, t) = Tr [S(\omega_0)\rho^{(1)}(t)], \quad (4.3)$$

if $\rho^{(1)}(t)$ denotes the matrix density of the total system; then with relation (4.2) one has

$$I_{Ab}(\omega_0, t) = -\frac{i}{\hbar} Tr \left\{ [V_0, C_0^+C_0] \rho^{(1)}(t) \right\}, \quad (4.4)$$

and it still can be expressed in the form

$$\begin{aligned} I_{Ab}(\omega_0, t) &= \frac{i}{\hbar} Tr \left\{ C_0^+C_0 [V_0, \rho^{(1)}(t)] \right\} \\ &= \frac{i}{\hbar} Tr \left\{ C_0^+C_0 L_{V_0} \rho^{(1)}(t) \right\}. \end{aligned} \quad (4.5)$$

Using the expression (3.11), the absorption spectrum can be expressed as

$$I_{Ab}(\omega_0, t) = \frac{i}{\hbar} Tr \left\{ [-V_{21} |2\rangle \langle 1| C_0 + V_{12} |1\rangle \langle 2| C_0^+] \rho^{(1)}(t) \right\}. \quad (4.6)$$

Here the trace is over the material system states and the field states, and we have used the invariance of the trace by circular permutation, and the rules of commutation of the operators of field C_0 and C_0^+ . We evaluate the trace from the system and the field states, i.e., $|1, N_0\rangle$ and $|2, N_0 - 1\rangle$. We then have

$$\begin{aligned} I_{Ab}(\omega_0, t) &= \frac{i}{\hbar} \left\{ -V_{21} \langle N_0 - 1 | C_0 | N_0 \rangle \langle 1, N_0 | \rho^{(1)}(t) | 2, N_0 - 1 \rangle \right. \\ &\quad \left. + V_{12} \langle N_0 | C_0 | N_0 - 1 \rangle \langle 2, N_0 - 1 | \rho^{(1)}(t) | 1, N_0 \rangle \right\}. \end{aligned} \quad (4.7)$$

The density matrix elements of $\rho^{(1)}(t)$ can be obtained directly from the perturbation calculation of relation (3.20). We mention that the stochastic operator $\Gamma_{S1212}(t)$ must be evaluated in the base of the total system. Under these conditions, the absorption spectrum is written

$$I_{Ab}(\omega_0, t) = \frac{2N_0 |V_{12}|^2}{\hbar^2} \left\{ \int_0^t dt_1 \exp \left[-\frac{i}{\hbar} \int_{t_1}^t d\tau (R_{1212}(\tau) + E_{12}) \right] + C.C. \right\}, \quad (4.8)$$

where the symbol $C.C.$ represents the complex conjugate part. If we note the stochastic coupling intervenes only between states having the same number of photons, then the energy of the field does not intervene. The matrix element $R_{1212}(t)$ was evaluated previously; it is given by relations (2.12) and (3.5). In the particular

case of our model, including the excited configuration only one radiant state and only one non-radiant state, its expression is reduced to

$$R_{1212}(t) = -i\hbar \left\{ \Gamma_{1212} + \frac{1}{2} (\delta\omega_{3223})^2 \frac{1 - \exp[-(\varepsilon_{3223} + i\omega_{23})t]}{\varepsilon_{3223} + i\omega_{23}} \right\}. \quad (4.9)$$

The absorption spectrum takes the form

$$I_{Ab}(\omega_0, t) = \frac{2N_0 |V_{12}|^2}{\hbar^2} Re \int_0^t d\tau \exp \left\{ \left[-\frac{i}{\hbar} E_{12} - \Gamma_{1212} - \frac{(\delta\omega_{3223})^2}{2(\varepsilon_{3223} + i\omega_{23})} \right] (t - t_1) \right\} \\ \times \exp \left\{ -\frac{(\delta\omega_{3223})^2}{2(\varepsilon_{3223} + i\omega_{23})^2} [\exp(-(\varepsilon_{3223} + i\omega_{23})t) - \exp(-(\varepsilon_{3223} + i\omega_{23})t_1)] \right\}, \quad (4.10)$$

where the general solution can be represented as a continued fraction. At this stage, we will note with the initial conditions we have fixed at $t = 0$, the steady state regime will be reached only for times longer than characteristic times of the material system defined by Γ_{1122}^{-1} and Γ_{1212}^{-1} . We will then obtain the general expression of the absorption spectrum, which will enable us to clarify the limit situations corresponding to white noise or fast fluctuations limit case. Taking into account the correlation function of (3.1), the white noise is characterized by the condition

$$\delta\omega_{3223} \ll \varepsilon_{3223}, \quad (4.11)$$

and in this case, the relation (4.10) takes the form

$$I_{Ab}(\omega_0, t) = \frac{2N_0 |V_{12}|^2}{\hbar^2} Re \int_0^t d\tau \exp \left\{ \left[-\frac{i}{\hbar} E_{12} - \Gamma_{1212} - \frac{(\delta\omega_{3223})^2}{2(\varepsilon_{3223} + i\omega_{23})} \right] (t - t_1) \right\}. \quad (4.12)$$

This expression results, on the one hand, from steady state regime for which

$$\exp(-\varepsilon_{3223}t) \leq \exp(-\varepsilon_{3223}t_1) \ll 1, \quad (4.13)$$

since the principal contribution to the integral is obtained when $t_1 \approx t$. But on the other hand, the white noise condition (4.11) allows one to obtain

$$\exp \left\{ -\frac{(\delta\omega_{3223})^2}{2(\varepsilon_{3223} + i\omega_{23})^2} [\exp(-(\varepsilon_{3223} + i\omega_{23})t) - \exp(-(\varepsilon_{3223} + i\omega_{23})t_1)] \right\} \approx 1. \quad (4.14)$$

After integration, we obtain for $t \rightarrow \infty$ the absorption spectrum in the white noise

$$I_{Ab}(\omega_0) = \frac{2N_0 |V_{12}|^2}{\hbar^2} \frac{\Gamma_{1212} + \frac{(\delta\omega_{3223})^2 \varepsilon_{3223}}{2(\varepsilon_{3223}^2 + \omega_{23}^2)}}{\left[\omega_0 - \omega_{21} - \frac{(\delta\omega_{3223})^2 \omega_{23}}{2(\varepsilon_{3223}^2 + \omega_{23}^2)} \right]^2 + \left[\Gamma_{1212} + \frac{(\delta\omega_{3223})^2 \varepsilon_{3223}}{2(\varepsilon_{3223}^2 + \omega_{23}^2)} \right]^2}, \quad (4.15)$$

which is quite similar to the one obtained in the frequency modulation case. We find a simple Lorentzian line shape centered at the natural frequency $\omega_0 = \omega_{21} + \frac{(\delta\omega_{3223})^2 \omega_{23}}{2(\varepsilon_{3223}^2 + \omega_{23}^2)}$, of which the contribution to the width at half maximum of line shape is

$$\gamma = (\delta\omega_{3223})^2 \frac{\varepsilon_{3223}}{\varepsilon_{3223}^2 + \omega_{23}^2}, \quad (4.16)$$

is lower than the amplitude of the correlation $\delta\omega_{3223}$. Moreover, one observes here additional motional narrowing effect in the absorption spectrum, which varies as a simple Lorentzian as a function of the detuning

frequency ω_{23} . Our result does reduce to Kubo [22] in absence of non-diagonal stochastic terms. Finally, we consider the second case associated with the colored noise or slow fluctuations limit defined by

$$\delta\omega_{3223} \gg \varepsilon_{3223}. \quad (4.17)$$

The discussion of this limit is more delicate because $\delta\omega_{3223}/\varepsilon_{3223}$ tends to infinity. Whereas the exponential in brackets in relation (4.10) tends to zero for sufficiently long times. In order to simplify the discussion, we note that the absorption spectrum $I_{Ab}(\omega_0, t)$ depends on the quantity

$$I(\omega_0) = \lim_{t \rightarrow \infty} \int_0^t f(t, t_1) g(t, t_1) dt_1, \quad (4.18)$$

where

$$f(t, t_1) = \exp \left\{ \left[-\frac{i}{\hbar} E_{12} - \Gamma_{1212} + \frac{i}{2} \frac{(\delta\omega_{3232})^2 \omega_{23}}{\varepsilon_{3223}^2 + \omega_{23}^2} - \frac{1}{2} \frac{(\delta\omega_{3223})^2 \varepsilon_{3223}}{\varepsilon_{3223}^2 + \omega_{23}^2} \right] (t - t_1) \right\}$$

$$g(t, t_1) = \exp \left\{ -\frac{(\delta\omega_{3223})^2}{2(\varepsilon_{3223} + i\omega_{23})^2} [\exp(-(\varepsilon_{3223} + i\omega_{23})t) - \exp(-(\varepsilon_{3223} + i\omega_{23})t_1)] \right\}. \quad (4.19)$$

Figure 2 shows the general shape of the real part of the term as a function of t_1 .

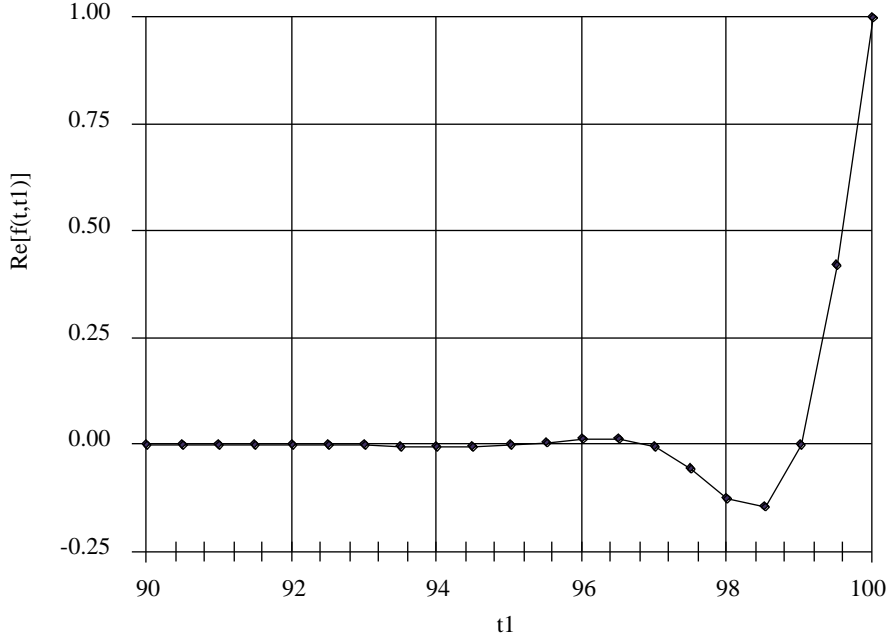


Figure 2. Variation of the real part of the $f(t, t_1)$ as a function of t_1 . Here, $t = 100$, $E_{12}/\hbar = 0$, $\omega_{23} = 0.32$, $(\delta\omega_{3223})^2 = 1$, $\varepsilon_{3223} = 0.01$, $\Gamma_{1212} = 1$.

To represent this curve, we have taken a finite time, in units of Γ_{1212} . The function takes significant values only in the vicinity of $t_1 \cong t$. It can be monotonic if $\omega_{23} = 0$ and $\frac{(E_2 - E_1)}{\hbar} = \omega_0$, or exhibit oscillations for nonzero values of the parameters. The limit of the $f(t, t_1)$ always equals one. Since this term appears under integral, more numerous are the oscillations, smaller the result will be. This term alone leads to a Lorentzian line shape. For finite times, the second term also presents oscillations when $\omega_{23} \neq 0$. The real part tends to one, whereas the imaginary part tends to zero when t tends to infinity. Also, in all cases, $g(t, t_1)$ is an increasing envelope function. Figure 3 shows the particular case where ε_{3223} is small and for which recurring oscillations typical of phenomena of memory appear.

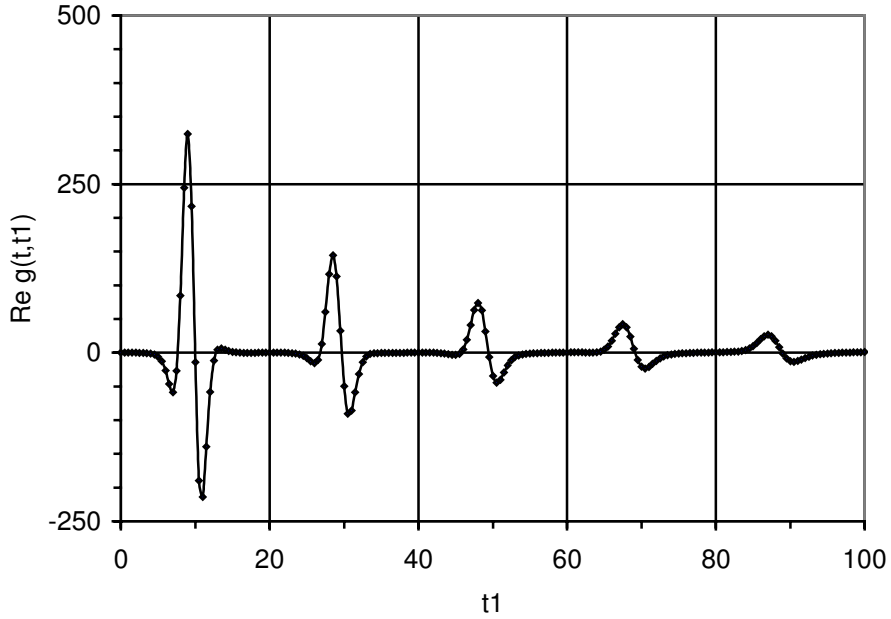


Figure 3. Variation of the real part of the $g(t, t_1)$ as a function of t_1 . $t = 100$, $E_{12}/\hbar = 0$, $\omega_{21} = 0.32$, $(\delta\omega_{3223})^2 = 1$, $\varepsilon_{3223} = 0.01$, $\Gamma_{1212} = 1$.

The product of the two terms contributes to the integral only for t_1 near t . When t_1 is near zero, the variation of the $f(t, t_1)$ takes over and the product remains very small, whatever the selected parameters. Figure 4 shows the product of the two terms represented in Figures 2 and 3.

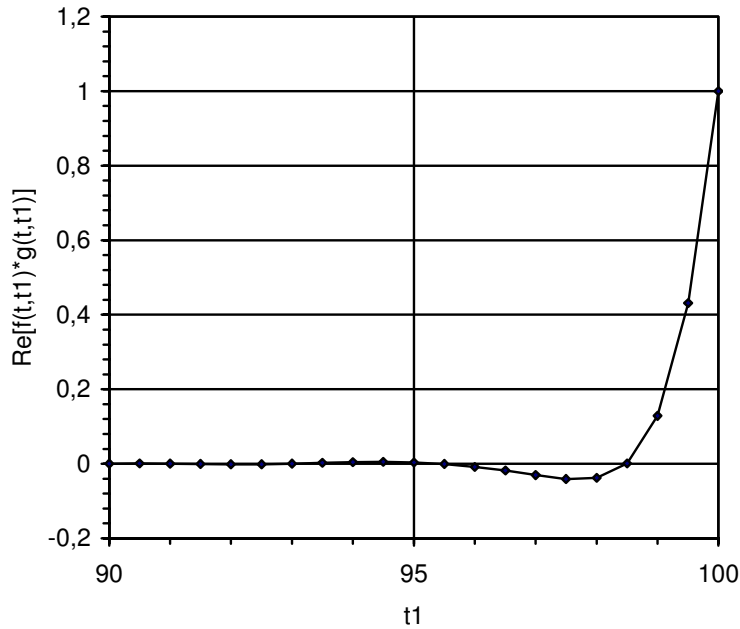


Figure 4. Variation of the real part of the product of the two terms $f(t, t_1)$ and $g(t, t_1)$ as a function of t_1 . $t = 100$, $E_{12}/\hbar = 0$, $\omega_{23} = 0.32$, $(\delta\omega_{3223})^2 = 1$, $\varepsilon_{3223} = 0.01$, $\Gamma_{1212} = 1$.

It can be noticed that the $g(t, t_1)$ still modifies clearly the form of $f(t, t_1)$ because t , although long, is finite. In fact, the absorption spectrum is defined only in the limit where t tends to infinity, because the

initial conditions were defined at $t = 0$. Consequently, one can put $g(t, t_1) = 1$ and take t long with respect to the inverse of the dephasing constant Γ_{1212}^{-1} of the system. It results from these observations that the line shape of the absorption spectrum in the presence of a non-diagonal stochastic interaction will be Lorentzian as in the other limit case. Its width at half maximum is given by

$$\delta = 2\Gamma_{1212} + \frac{(\delta\omega_{3223})^2 \varepsilon_{3223}}{\varepsilon_{3223}^2 + \omega_{23}^2}. \quad (4.20)$$

In addition, the frequency shift $\Delta\omega$ is given by

$$\Delta\omega = -\frac{1}{2} \frac{(\delta\omega_{3223})^2 \omega_{23}}{\varepsilon_{3223}^2 + \omega_{23}^2}, \quad (4.21)$$

when $\omega_{23} \neq 0$. Figure 5 shows three typical situations: (a) natural line width in the absence of stochastic interaction, (b) line broadened by stochastic interaction and (c) line broadened and shifted in frequency.

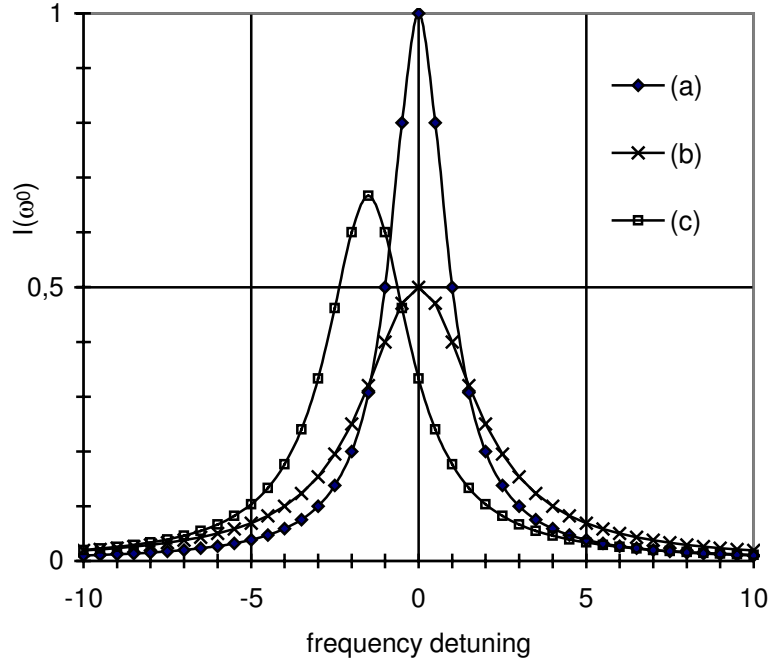


Figure 5. we represent the variation of the absorption spectra $I(\omega_0)$ as a function of frequency detuning $(\omega_0 - \omega_{12})$ for different cases

- (a) $\omega_{23} = 0.$, $(\delta\omega_{3223})^2 = 0.$, $\varepsilon_{3223} = 1.$, $\Gamma_{1212} = 1.$
- (b) $\omega_{23} = 0.$, $(\delta\omega_{3223})^2 = 2.$, $\varepsilon_{3223} = 1.$, $\Gamma_{1212} = 1.$
- (c) $\omega_{23} = 0.32.$, $(\delta\omega_{3223})^2 = 10.$, $\varepsilon_{3223} = 1.$, $\Gamma_{1212} = 1.$

5. Conclusion

In this article, we have presented a general formalism to describe a material system coupled to a heat bath and undergoing stochastic perturbations. We have assumed the heat bath purely quantum in nature, generates relaxation and dephasing processes.

For such systems, by taking advantage of a general formalism presented in paper [8], and to extend it more complex systems, we have developed a stochastic approach which enables us to study how the stochastic interaction acting on the excited states of the system affect the dynamical evolution. Our description is valid

for diagonal and non-diagonal interaction. Also, dephasing processes have been introduced in the model. This point is of particular interest since the important role by coherence effects in non-radiative decay has been demonstrated [32]. For this purpose, we have considered a system of which the excited radiant state is coupled stochastically to a non-radiant state of a lower electronic configuration. In this case, we have determined the absorption spectrum in the white noise and colored noise limits. In addition, we have found the line shape for stochastic non-diagonal perturbations to remain Lorentzian. This result is different from the case of motional-narrowing limit of frequency modulation where a transition from a Gaussian to a Lorentzian line shape can be observed. It would be interesting to be able to extend our study if one would have not one, but an ensemble of isoenergetic non-radiant states with excited state radiant.

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