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NON MARKOVIAN UNIFIED THEORY OF DEPHASING IN TWO-PHOTON AND MULTIPHOTON PROCESSES

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INTRODUCTION

A general formalism was developed recently towards the microscopic calculation of dephasing phenomena in multiphoton processes.[1-3] We present here the exact solution of a stochastic model for dephasing in two photon processes. Our solution accounts in a unified way for a variety of dephasing processes in the material system (collisional, phonon induced, density fluctuations in condensed phases, etc.) as well as dephasing induced by phase fluctuations of the radiation fields. The key quantity in our theory is a four point correlation function of the dipole operator $F(\tau_1,\tau_2,\tau_3)$. We derive a general expression for F which is not restricted to the Markovian limit and show how the various types of dephasing correspond to special cases of F. Both time-resolved and frequency-resolved experiments are examined. We further present an approximate expression for fluorescence line shapes in a strong field and for the nonlinear susceptibility $\chi^{(3)}$, obtained using the factorization approximation.[2] The latter approximation allows us to express multiphoton line shapes in terms of single photon line shape functions, for which a microscopic theory is readily available.

We consider a three level system |a>, |b> and |c> undergoing a fluorescence process in which the material system initially at state |a> absorbs an ω_L photon and goes via the intermediate state |b> to

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$|c\rangle$, with the emission of an ω_s photon. The detunings of the fields from the material level frequencies are $\Delta_L \equiv \omega_L - \omega_{ba}$, $\Delta_s \equiv \omega_s - \omega_{bc}$. Our stochastic hamiltonian in the rotating wave approximation which accounts for the most general dephasing processes allowed in this system is:

$$\begin{aligned} H = & [\Delta_L + \delta\bar{\omega}_{ab}(t)]\ (|a\rangle\langle a| - |b\rangle\langle b|) \\ & + [\Delta_s + \delta\omega_{bc}(t)]\ (|b\rangle\langle b| - |c\rangle\langle c|) \\ & + \mu_L\ \Psi(t)\ (|a\rangle\langle b| + |b\rangle\langle a|) + \mu_s(|b\rangle\langle c| + |c\rangle\langle b|) \\ & - \frac{i}{2}\gamma_a\ |a\rangle\langle a| - \frac{i}{2}\gamma_b\ |b\rangle\langle b| - \frac{i}{2}\gamma_c\ |c\rangle\langle c| \end{aligned} \tag{1}$$

Here γ_ν^{-1} is the inverse lifetime of level ν and μ_L and μ_s are the dipole matrix elements. $\Psi(t)$ is the envelope of an external field (E_L) with frequency ω_L

$$E_L(t) = \Psi(t)\ \exp(i\omega_L t)\ \exp[i\int_0^t d\tau\ \delta\omega_L(\tau)] + c.c. \tag{2}$$

$\delta\omega_L(\tau)$ denotes a stochastic modulation of the phase of the field. $\delta\bar{\omega}_{ab}(t)$ and $\delta\omega_{bc}(t)$ are two stochastic processes which describe the modulation of the interlevel frequencies in the material system. It will be shown below that $\delta\omega_L(t)$ and $\delta\bar{\omega}_{ab}(t)$ actually play the same role. We shall therefore define:

$$\delta\omega_{ab}(\tau) \equiv \delta\bar{\omega}_{ab}(\tau) + \delta\ \omega_L(\tau)\ . \tag{3}$$

We further assume that $\langle\delta\omega_{ab}\rangle = \langle\delta\omega_{bc}\rangle = 0$ where the $\langle....\rangle$ comes for averaging over the stochastic processes. Our stochastic model will be determined by specifying the two time self correlation functions $\langle\delta\omega_{ab}(0)\delta\omega_{ab}(\tau)\rangle$, $\langle\delta\omega_{bc}(0)\delta\omega_{bc}(\tau\rangle$ and the cross correlation function $\langle\delta\omega_{ab}(0)\delta\omega_{bc}(\tau)\rangle$. We shall therefore define the following quantities which are simply the double-integrals of these correlation functions:[1]

$$g_{ab}(\tau) \equiv \int_0^\tau d\tau_1(\tau-\tau_1)\ \langle\delta\omega_{ab}(0)\ \delta\omega_{ab}(\tau_1)\rangle, \tag{4a}$$

$$g_{ba}(\tau) \equiv \int_0^\tau d\tau_1(\tau-\tau_1)\ \langle\delta\omega_{bc}(0)\ \delta\omega_{bc}(\tau_1)\rangle, \tag{4b}$$

$$g_{abc}(\tau) \equiv \int_0^\tau d\tau_1(\tau-\tau_1)\ \langle\delta\omega_{ab}(0)\ \delta\omega_{bc}(\tau_1)\rangle. \tag{4c}$$

In addition, we introduce $g_{ac}(\tau)$ the correlation function of fluctuations in ω_{ac}. Since $\delta\omega_{ac} = \delta\omega_{ab} + \delta\omega_{bc}$ we have:

$$g_{ac}(\tau) \equiv \int_0^\tau d\tau_1(\tau-\tau_1)\ \langle\delta\omega_{ac}(0)\delta\omega_{ac}(\tau)\rangle = g_{ab}(\tau) + g_{bc}(\tau) + 2\ g_{abc}(\tau) \qquad (5)$$

We shall further assume that the processes $\delta\omega_{ab}(\tau)$ and $\delta\omega_{bc}(\tau)$ are Gaussian. This implies that all higher order correlation functions $\langle\delta\omega\delta\omega\delta\omega\delta\omega\rangle$ etc. can be expressed in terms of $g(\tau)$ (eqs. 4). However, we need not assume that the processes are Markovian and $g(\tau)$ can assume any form. In the Markovian limit $\langle\delta\omega(\tau)\delta\omega\rangle$ are δ functions in τ and $g(\tau)$ are linear in τ $g(\tau) = \Gamma|\tau|$.

It was shown recently[1-3] that any two photon lineshape associated with the hamiltonian (eq. 1) can be expressed in terms of the following four-time correlation function:

$$F(\tau_1,\tau_2,\tau_3)\ \langle V_{ab}(0)\ V_{bc}(\tau_1)\ V_{cb}(\tau_2)\ V_{ba}(\tau_3)\rangle \qquad (6)$$

where

$$V_{ab}(\tau) = |a\rangle\langle b|\ \mu_L\ \exp(i\int_0^\tau d\tau_1\,\delta\omega_{ab}(\tau_1)) \qquad (6a)$$

and

$$V_{bc}(\tau) = |b\rangle\langle c|\ \mu_s\ \exp(i\int_0^\tau d\tau_1\,\delta\omega_{bc}(\tau_1)) \qquad (6b)$$

In a <u>steady state</u> experiment ($\Psi(t) = 1$ in eq. 1) the rate for the absorption of ω_L and the emission of ω_s is:

$$I(\Delta_L,\Delta_s) = \mu_L^2\mu_s^2 \int_0^\infty d\tau_1 \int_0^{\tau_1} d\tau_2 \int^{\tau_2} d\tau_3$$

$$[\phi(\tau_1,\tau_2,\tau_3)F(\tau_1,\tau_2,\tau_3) + \phi(\tau_2,\tau_1,\tau_3)F(\tau_2,\tau_1,\tau_3) \qquad (7)$$

$$-\frac{1}{2}\gamma_b(\tau_1+\tau_2-\tau_3) - \frac{1}{2}\gamma_c|\tau_1-\tau_2|]. \qquad (7a)$$

The emission rate of photon ω_s at time t in <u>time resolved</u> experiments is given by:

$$\hat{I}(t,\Delta_L,\Delta_s) = \mu_L^2\mu_s^2 \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3$$

$$F(t-\tau_3,\tau_1-\tau_3,\tau_2-\tau_3)\phi(t-\tau_3,\tau_1-\tau_3,\tau_2-\tau_3)\Psi(\tau_2)\Psi(\tau_3)$$
$$+ F(\tau_1-\tau_3,t-\tau_3,\tau_2,\tau_3)\phi(\tau_1-\tau_3,t-\tau_3-\tau_2-\tau_3)\Psi(\tau_2)\Psi(\tau_3) \quad (8)$$
$$+ F(\tau_2-\tau_3,t-\tau_3,\tau_1-\tau_3)\phi(\tau_2-\tau_3,t-\tau_3,\tau_1-\tau_3)\Psi(\tau_2)\Psi(\tau_3).$$

It should be noted that $\hat{I}(t,\Delta_L,\Delta_t)$ as defined in eq. (8) is not an observable quantity since it corresponds to an unrealistic measurement with infinite temporal and frequency resolution. Any realistic detector will contain a finite temporal and spectral resolution and these should be convoluted with $I(t,\Delta_L,\Delta_s)$ to get the actual result (I_{exp}) of a particular measurement.

$$\hat{I}_{exp}(t,\Delta_L,\Delta_s) = \int d\tau \int d\Delta \quad (9)$$
$$\hat{I}(t+\tau,\Delta_L+\Delta,\Delta_s)\phi_D(\Delta,\tau)$$

$\phi_D(\Delta,\tau)$ being a detector function.[4] Using the hamiltonian (eq. 1), the exact solution for $F(\tau_1,\tau_2,\tau_3)$ is[1]

$$F(\tau_1,\tau_2,\tau_3) = \exp[-g_{ab}(\tau_3) - g_{bc}(\tau_1-\tau_2)$$
$$- g_{abc}(\tau_1) - g_{abc}(\tau_3-\tau_2) + g_{abc}(\tau_2) + g_{abc}(\tau_3-\tau_1)] \quad (10)$$

Eqs. (7) and (8) together with eq. (6) and (10) constitute our most general expression for two-photon lineshapes. We note that these expressions are the same regardless of the specific dephasing mechanism. The only differences can come from the specific form of $g_{\nu\mu}(\tau)$. Let us consider now separately the cases of field fluctuations and level fluctuations.

Field Fluctuations

Assuming that $\delta\omega_L \neq 0$ $\gamma\omega_{ab} = \delta\omega_{bc} = 0$ we have $g_{bc}(\tau) = g_{abc}(\tau) = 0$ and

$$F(\tau_1,\tau_2,\tau_3) = \exp[-g_{ab}(\tau_3)] \quad (11)$$

Upon the substitution of eq. (11) in eqs. (7) and (8) we get the results of field fluctuations. These can be written in a more compact way by defining the power spectrum of the field

$$J(\Delta) \equiv \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\tau \exp(i\Delta\tau - g_{ab}(\tau)) \quad (12)$$

We further define $I_o(\Delta_L,\Delta_s)$ and $\hat{I}_o(t,\Delta_L,\Delta_s)$ to be the Raman cross sections (eqs. (7) and (8) respectively) in the absence of any dephasing ($g_{\nu\mu}(\tau) = 0$ and $F = 1$). We then have

$$\hat{I}(\Delta_L, \Delta_s) = \int d\Delta \; \hat{I}_o(\Delta_L + \Delta, \Delta_s) \; J(\Delta) \tag{13a}$$

$$\hat{I}(t, \Delta_L, \Delta_s) = \int d\Delta \; I_o(t, \Delta_L + \Delta, \Delta_s) J(\Delta) \tag{13b}$$

The entire effect of field fluctuations is therefore simply to convolute the line shapes with $J(\Delta)$.

Level Fluctuations

Here the correlation functions (4) will depend on the specific interactions with the bath. A simple choice could be that levels $|a\rangle$ and $|c\rangle$ have similar interactions with the bath so that $\delta\omega_{ab}(\tau) = \gamma\omega_{cb}(\tau)$. This will be the case in a two level system (level $|c\rangle$ is identical with level $|a\rangle$)[5] or in molecular processes where $|a\rangle$ and $|c\rangle$ are two vibrational states belonging to the ground electronic state whereas $|b\rangle$ is an electronically excited state. In this case $g_{ab}(\tau) = g_{bc}(\tau) = g_{abc}(\tau) \equiv g(\tau)$, and we get

$$F(\tau_1, \tau_2, \tau_3) = \exp[-g(\tau_3) - g(\tau_1 - \tau_2) - g(\tau_1) - g(\tau_3 - \tau_2) + g(\tau_2) + g(\tau_3 - \tau_1)]. \tag{14}$$

The Factorization Approximation

The triple Fourier transform in eqs. (7) and (8) can be evaluated in a closed form only for simple cases (e.g. the Markovian limit in which $g_{\nu\mu}(\tau)$ are linear in τ). It may be therefore helpful to introduce some approximate solutions. Such an approximation scheme was developed recently.[2,3] It enables us to express the cross section for any multiphoton process (for which the present two photon problem is a special case) in terms of single photon line shape functions. The complex generalized line shape function for the $\nu\mu$ transition is defined as follows:

$$I_{\nu\mu}(\omega) \equiv -i \int_0^\infty d\tau \exp(-i\omega\tau) \exp[-i\omega_{\nu\mu} - \frac{1}{2}(\gamma_\nu + \gamma_\mu)\tau - g_{\nu\mu}(\tau)] \tag{15}$$

where $\omega_{\nu\mu} \equiv \varepsilon_\mu - \varepsilon_\mu$ is the frequency of the $\nu\mu$ transition. The imaginarty part of I is the ordinary absorption line shape between levels ν and μ and will be denoted I". I may be calculated from I" using the Kramer Kronig relations. The approximate solution for $I(\Delta_L, \Delta_s)$ within the factorization approximation is:[2]

$$\hat{I}(\Delta_L, \Delta_s) = 2\mu_L^2 \mu_s^2 \left\{ \frac{2}{\gamma_b} I''_{ab}(\Delta_L) I''_{cb}(\Delta_s) \right.$$

$$+ \mathrm{Im}[I^*_{ac}(\Delta_L-\Delta_s)\, I_{cb}(\Delta_s) I^*_{ab}(\Delta_L)] \Big\} \quad (16)$$

We have further derived the following expression for the fluorescence in a three level system in a <u>strong</u> radiation field using the factorization approximation:

$$\hat{I}(\Delta_L,\Delta_s) = \frac{2\mu_L^2\mu_s^2}{1 + (4\mu_L^2/\gamma_b) I''_{ab}(\Delta_L)} \Bigg\{ \frac{2}{\gamma_b} I''_{ab}(\Delta_L) I''_{cb}(\Delta_s)$$

$$+ \mathrm{Im}\left[\frac{1}{[I^*_{ac}(\Delta_L-\Delta_s) I_{cb}(\Delta_s)]^{-1} + \mu_L^2}\left[I^*_{ab}(\Delta_L) + \frac{2\mu_L^2}{\gamma_b} I''_{ab}(\Delta_L) I''_{cb}(\Delta_s)\right]\right]\Bigg\} \quad (17)$$

This expression is valid both for field fluctuations whereby $g_{ab}(\tau) = g_{ac}(\tau)$ and $g_{bc}(\tau) = 0$ and for general level fluctuations (eq. 4). Fig. 1 shows $I(\Delta_L,\Delta_s)$ (eq. 17). For $I_{\nu\mu}(\omega)$ we have used the stochastic line shape function of Kubo[6] given by eq. 15 with

$$g_{\nu\mu}(\tau) = \frac{\delta^2}{\Lambda^2}[\exp(-\Lambda\tau) - 1 + \Lambda\tau] \quad (18)$$

Here δ is the amplitude of fluctuations and Λ^{-1} is their inverse time scale. Defining $\kappa \equiv \Lambda/\delta$ then as $\kappa\to\infty$ $I''_{\nu\mu}(\omega)$ will assume a Lorenzian form with width δ^2/Λ whereas for $\kappa\to 0$ $I''_{\nu\mu}(\omega)$ becomes a Gaussian with width $\sim\delta$. In Fig. 1 we display our results. The right column is in the Markovian limit (I" is Lorentzian) whereas the left column is highly non Markovian (I" is Gaussian).

<u>Non Markovian Theory for Nonlinear Susceptibilities</u>

Within the factorization approximation we have recently derived an expression for the nonlinear susceptibility $\chi^{(3)}$ which is valid also at large detunings (non Markovian region)[3]

$$\chi^{(3)}(-\omega_4,\omega_1,-\omega_2,\omega_3) = \sum_{a,b,c,d} \bar{P}(a) \sum_{P(\omega_1,-\omega_2,\omega_3)}$$

$$\begin{aligned}
[- & I_{ad}(\omega_1-\omega_2+\omega_3)\ I_{ac}(\omega_1-\omega_2)\ I_{ab}(\omega_1) \\
+ & I_{dc}(\omega_1-\omega_2+\omega_3)\ I_{db}(\omega_1-\omega_2)\ I_{da}(\omega_1) \\
+ & I_{dc}(\omega_1-\omega_2+\omega_3)\ I_{db}(\omega_1-\omega_2)\ I_{ab}(\omega_1) \\
+ & I_{dc}(\omega_1-\omega_2+\omega_3)\ I_{ac}(\omega_1-\omega_2)\ I_{ab}(\omega_1) \\
+ & I_{ba}(\omega_1-\omega_2+\omega_3)\ I_{ca}(\omega_1-\omega_2)\ I_{da}(\omega_1) \\
- & I_{cb}(\omega_1-\omega_2+\omega_3)\ I_{db}(\omega_1-\omega_2)\ I_{ab}(\omega_1) \\
- & I_{cb}(\omega_1-\omega_2+\omega_3)\ I_{db}(\omega_1-\omega_2)\ I_{da}(\omega_1) \\
- & I_{cb}(\omega_1-\omega_2+\omega_3)\ I_{ca}(\omega_1-\omega_2)\ I_{da}(\omega_1)].
\end{aligned} \tag{19}$$

Here $\bar{P}(a)$ is the equilibrium population of level $|a\rangle$ and $P(\omega_1,-\omega_2,\omega_3)$ stands for the sum over all permutations of these three fields. The summation over b, d runs over all excited levels, $\chi^{(3)}$ describes a coherent process whereby photons ω_1 and ω_3 are absorbed, a photon ω_2 is emitted and a fourth field ω_4 is being generated. In the Markovian limit we assume $g_{\nu\mu}(\tau) = \Gamma_{\nu\mu}|\tau|$ $I_{\nu\mu}(\omega)$ becomes Lorentzian and eq. (19) reduces to the well known 48 term expression of Bloembergen et al.[7]

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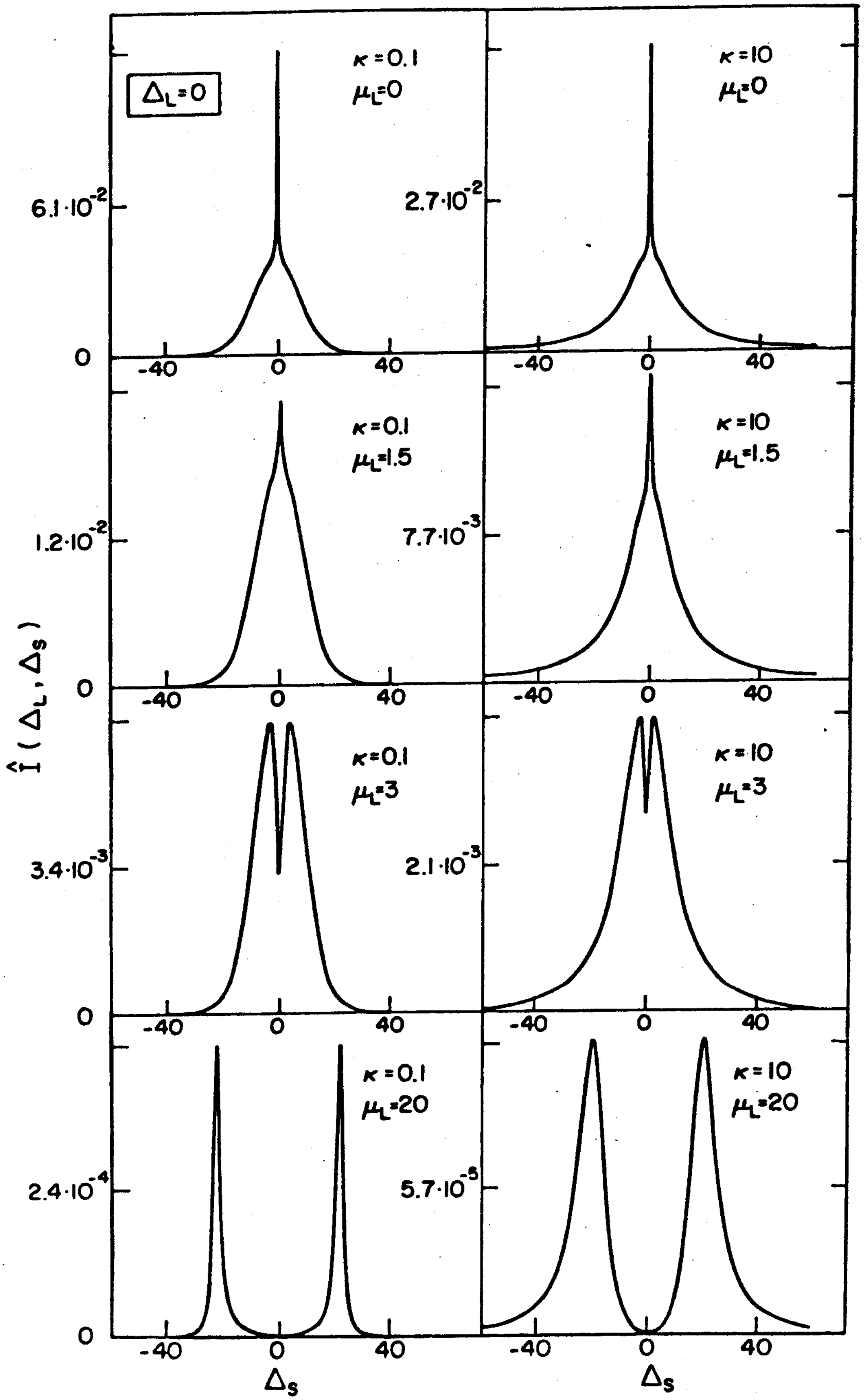

Fig. 1 Resonance Raman line shape of a three level system in a strong pump field[2]. The right column is for the Markovian limit and the left column is for non Markovian lineshapes.