Effective Hamiltonian for $SaS$ pairs generation with pump and probe polarized modes

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(Dated: June 16, 2020)

In the correlated Stokes-anti–Stokes scattering ($SaS$) an incident photon interacts with a Raman-active material, creating a Stokes photon and exciting a quantum vibrational mode in the medium, which is posteriorly annihilated on contact with a second incident photon, producing in turn an anti-Stokes photon. This can be accomplished by real and virtual processes. In real process the quantum mode shared between the Stokes and anti-Stokes events is a real particle, whereas in virtual processes the pair formation is mediated by the exchange of virtual particles. Here, we introduce a Hamiltonian to describe the pair production in $SaS$ scattering, for both types of process, when stimulated by two orthogonally polarized laser pulses in a pump-and-probe configuration. We also model the effect of the natural decay of the vibration created in the Stokes event and compute the probability of producing $SaS$ pairs. Additionally, we follow the dynamics of the vibration by considering the Stokes and anti-Stokes fields as external reservoirs, obtaining thus a master equation for the reduced density matrix for the vibrational population. Finally, we compare our theoretical results with recently published experimental data.

I. INTRODUCTION

The Raman spectrum of materials arises as a consequence of the inelastic scattering of light by matter [1] which is underlaid on two types of process: the Stokes process ($S$), characterized by the annihilation of an incoming photon of frequency $\omega_L$ and the creation of a redshifted photon of frequency $\omega_S$ together with the excitation of a quantum vibrational mode of frequency $\nu$ in the target medium; and the anti-Stokes process ($aS$), where the incident photon and an existing vibration are annihilated, generating a blueshifted photon of frequency $\omega_{aS}$. In each event, energy is conserved such that the frequency of the outgoing photon is equal to the frequency of the pump plus ($aS$) or minus ($S$) that of the vibration. As proposed by Klyshko [2,3], an additional process is also possible: the correlated Raman scattering, or Stokes-anti-Stokes process ($SaS$). In this case, the overall scattering involves the annihilation of two incoming photons of frequency $\omega_L$ and the creation of a pair composed of one Stokes and one anti-Stokes photon, such that $\omega_S + \omega_{aS} = 2\omega_L$. The non-classical nature of the correlated Stokes–anti-Stokes Raman scattering components has been demonstrated experimentally by several authors [4,11].

Such correlated $SaS$ pairs can involve the exchange of a real vibration, created in a Stokes process and subsequent destroyed by an anti-Stokes one. In this case, not only does the above mentioned overall energy conservation holds, but the pair is created red and blue shifted with respect to the incoming laser energy by the vibrational mode frequency, i.e. each Stokes and anti-Stokes photon has a well defined frequency $\omega_{aS,S} = \omega_L \pm \nu$. These pairs, here addressed as real $SaS$, lie at the core of recent pump-and-probe experiments exploiting the vibrations of the material as a potential quantum memory, and are characterised by a time correlation dominated by the lifetime $\tau_p$ of such vibrational modes. In solids, these vibrations are phonons of typical lifetimes of a few picoseconds [4,11,12,13] and have led to new experiments to store and process classical and quantum information on picosecond time-scales at room temperature with several different materials [4,14,20].

The correlated Raman scattering also takes place out of resonance, as demonstrated in Ref. [8]. In the denominated virtual processes, the energy of $S$ and $aS$ events are tuned out of resonance with the vibrational mode, so that the generation of photon pairs happens by means of the exchange of virtual vibrations. The photon pair produced by a virtual process can be viewed as the photonic analogue of the Cooper pairs in superconductivity [21]. Some properties of the so-called photonic Cooper pairs, or PCP, were studied in [11,22] for open air propagation and their existence has also been predicted for waveguides in [23]. While the real $SaS$ process has a characteristic timescale dictated by the phonon lifetime, as previously observed in different studies, in the virtual $SaS$ process the exchange of virtual phonons is expected to be nearly instantaneous, therefore limited only by the inverse bandwidth of the excitation pump pulse.

This scattering time difference was experimentally demonstrated in [13] in a time-delayed pump and probe setup with pulses of orthogonal polarization. The real $SaS$ data was fit with a phenomenological model that assumed a probability to create an anti-Stokes photon by the probe, conditioned on the creation of a Stokes photon by the pump and an exponential decay of the phonon population. The description of the virtual $SaS$ assumed simultaneity of the pair creation, limited by the
inverse linewidth of the pump pulse, as above mentioned. In this paper, we use an extension of the model proposed in \[24\] to provide a unified theoretical framework for the creation of pairs through either virtual or real vibration exchange. We calculate the time evolution of the overall quantum state of both photonic and vibrational fields and obtain the probability distribution of $S_a S$ pairs generation considering the natural decay of the vibrations in the material. We also consider the Stokes and anti-Stokes fields as creating and absorbing reservoirs for the vibrations and derive a master equation for its dynamics. We use both approaches to fit the data in \[13\] and to test the validity of the phenomenological model used therein.

II. GENERAL THEORETICAL FRAMEWORK

Our stating point is the effective Hamiltonian proposed in Ref. \[24\], given by

$$H = \hbar \omega_L a^\dagger a + \hbar v c^\dagger c + \hbar \omega_S b^\dagger_S b_S + \hbar \omega_{as} b^\dagger_{as} b_{as} + \hbar \lambda_S \left( ab^\dagger_S c^\dagger + H.c. \right) + \hbar \lambda_{as} \left( ab^\dagger_{as} c + H.c. \right), \quad (1)$$

where $b^\dagger_S (b_S)$, $b^\dagger_{as} (b_{as})$, $c^\dagger (c)$ and $a^\dagger (a)$ stand for the creation operator of $S$, $a S$, phonon and incident fields, respectively. The constant $\lambda_S$ ($\lambda_{as}$) denotes the coupling between the laser and the material, responsible for the Stokes (anti-Stokes) events. The Stokes and anti-Stokes photon frequencies are given by $\omega_{S,as} = \omega_L \mp \nu$, for real processes, with $\omega_L$ and $\nu$ being the pump and phonon frequencies, respectively. The Hamiltonian is obtained by handling the Raman scattering as an optical parametric amplification process \[25\]. It is valid within the coherence time of the pumping laser, whether continuous or pulsed. Our procedure is also similar to the one used in Ref. \[10\].

A. Full dynamics for the quantum fields

In \[1\], the pump laser is assumed to be a quantum field but, given its very large power and the relatively low count of Raman photons, its depletion can be ignored and it can be replaced by a classical function of time. We are, then, left with three quantum fields whose dynamics we proceed to calculate, the Stokes and anti-Stokes photonic modes and the phonon of the material.

First, we extend Hamiltonian \[1\] to the case in which the $S_a S$ process is stimulated by the incidence of two orthogonally polarized laser pulses, and the Stokes and anti-Stokes fields can be generated at arbitrary frequencies. The total Hamiltonian describing the dynamics of pair generation, then, reads

$$H(t) = \hbar v c^\dagger c + H_{0n} + H_{0v} + H_{I_H}(t) + H_{I_V}(t). \quad (2)$$

The first term is, once again, the free energy of the vibrational mode, whereas the second and third terms, given by

$$H_{0H(V)} = \int_0^\infty d\omega \rho(\omega) \hbar \omega b^\dagger_{S_{(V)}}(\omega) b_{S_{(V)}}(\omega)$$

$$+ \int_0^\infty d\sigma \rho(\sigma) \hbar \sigma b^\dagger_{aS_{(V)}}(\sigma) b_{aS_{(V)}}(\sigma), \quad (3)$$

are the free energy of the photonic Stokes and anti-Stokes fields for the two orthogonal polarizations of the pump. $\rho(\omega)$ is the density of states as a function of the frequency. Finally, the two last terms describe the coupling of all the fields via the material, and read

$$H_{I_H}(t) = \int_0^\infty d\omega g(\omega) f_H(t - t_0) b^\dagger_{S_{(V)}}(\omega) c^\dagger$$

$$+ \int_0^\infty d\sigma g(\sigma) f_H(t - t_0) b^\dagger_{aS_{(V)}}(\sigma)c + h.c., \quad (4)$$

$$H_{I_V}(t) = \int_0^\infty d\omega g(\omega) f_V(t - t_1) b^\dagger_{S_{(V)}}(\omega) c^\dagger$$

$$+ \int_0^\infty d\sigma g(\sigma) f_V(t - t_1) b^\dagger_{aS_{(V)}}(\sigma)c + h.c., \quad (5)$$

where $g(\omega)$ gives the coupling between pump, created photon at frequency $\omega$ and the vibrational mode. $f_H(t - t_1)$ describes the amplitude of the pump field and we assume that the converted photons preserve the polarization of the pump field, a hypothesis justified by the experiment we want to explain \[13\].

So far, the model is generic and could describe a myriad of experiments. However, our target here is the data obtained in \[13\] and that is why, from now on, we will describe the coupling terms in the interaction picture by

$$\tilde{H}_{I_H} = \alpha_H e^{-\frac{(t-t_0)^2}{\Delta_1^2}} \left[ \int_0^\infty d\omega g(\omega) e^{i\Delta_1 t} b^\dagger_{S_{(V)}}(\omega)c^\dagger + \int_0^\infty d\sigma g(\sigma) e^{i\Delta_1 t} b^\dagger_{aS_{(V)}}(\sigma)c + h.c. \right], \quad (6)$$

$$\tilde{H}_{I_V} = \alpha_V e^{-\frac{(t-t_1)^2}{\Delta_2^2}} \left[ \int_0^\infty d\omega g(\omega) e^{i\Delta_2 t} b^\dagger_{S_{(V)}}(\omega)c^\dagger + \int_0^\infty d\sigma g(\sigma) e^{i\Delta_2 t} b^\dagger_{aS_{(V)}}(\sigma)c + h.c. \right], \quad (7)$$

where $\Delta_1 = \omega_L - \omega - \nu$ and $\Delta_2 = \omega_L - \sigma + \nu$. We are, thereby, following the experimental setup that features two consecutive Gaussian pulses of orthogonal polarizations, each centered at the same frequency $\omega_L$, of time width $\Delta t$ and time delayed by $\delta t = t_1 - t_0$.

After being created, the photonic fields propagate freely and will be eventually collected by the detectors. The phonon, however, can decay, e.g. due to its interaction with other vibrations of the material. Therefore, its dynamics, and by consistency, that of the entire system, is not unitary and cannot be properly described by solving the Schroedinger equation with Hamiltonian \[2\]. In order to take the vibrational decay into consideration,
we calculate the dynamics of the system by solving the following master equation (in the interaction picture):

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} \left[ \hat{H}_I(t) + \hat{H}_V(t), \rho \right] + \mathcal{L}(\rho), \quad (8)$$

where $\rho$ is the density operator for all the quantum fields (Stokes, anti-Stokes and phonon) and the Lindblad term $\mathcal{L}(\rho)$ is given by

$$\mathcal{L}(\rho) = \gamma \left( 2c\rho c^\dagger - c^\dagger c\rho - \rho c^\dagger c \right), \quad (9)$$

with $\gamma$ being the decay rate (proportional to the inverse of the lifetime) of the vibrational field. This equation assumes a dissipative channel at zero temperature which is a good approximation for the experiment performed in [13], where the vibration corresponds to an optical phonon whose average number of thermal excitations at room temperature is of the order of $10^{-3}$. The integration in time of Eq. (5) gives the general solution for our system. A similar approach for the vibrational dynamics in the context of Raman scattering was used in [20].

There, however, the scattering involves plasmons in a cavity whereas here it happens in free space.

**B. Master equation for the phonon population**

Eq. (8) of the previous subsection contains all the information about the dynamics of each quantum field involved in the scattering process, as well as any eventual time correlation among them. However, the phenomenological approach used in [13] considers that the time-delayed cross-correlation function of $SaS$ pairs can be obtained essentially from the time dependence of the vibrational population. The underlying assumptions are that the real $SaS$ processes that mostly contribute for the pair counting are those where the correlation is driven solely by the shared phonon (i.e. the individual scattering processes are statistically independent) and that each event is very rare. In other words, the Stokes process is spontaneous (the vibrational field is basically in the vacuum at the arrival of each pump pulse), in each pulse at most one phonon is excited (Stokes processes are rare), and when the anti-Stokes process takes place it is solely due to the phonon created within the same pump-probe pair. All these assumptions meet the experimental conditions. First, the time distance between pairs of pump-probe pulses (13 ns) is much larger than the decay time of phonons in the material (few picoseconds) and, as mentioned before, the average number of thermal phonons is very low (around $10^{-3}$), thus justifying the first assumption of pump pulses reaching the material in its vacuum state of phonons. Second, the rate of Stokes photons is of the order of $10^4$ counts per second, while the pulses strike the material at around 76 MHz, which means that each pulse has a probability smaller than $10^{-3}$ of creating a Stokes photon and, hence, a phonon. Finally, in order to guarantee the absolute statistical independence of the real $SaS$ pairs, the detection post-selects Stokes and anti-Stokes photons of orthogonal polarizations, each sharing the polarization respectively of the pump and the probe pulses. That guarantees that the Stokes comes from the pump and the anti-Stokes from the probe.

The robustness of the model described in the previous subsection also relies on the fact that it allows to derive an equation exclusively for the dynamics of the phonons themselves. As we proceed to show, under the circumstances of the performed experiment, when discussing the phonons alone, Stokes and anti-Stokes fields play the role of external reservoirs. The Stokes field will correspond to a pumping reservoir that incoherently creates phonons in the material, while the anti-Stokes field will enhance the dissipation rate of such phonons. Given the typical time scales of the pulses and the weakness of individual scattering processes, we will proceed to derive a master equation for the phonons taking into account these extra reservoirs. As it will become clear soon, the time dependence of the pulse will reflect in time dependent dissipative or pumping rates.

To get an expression for the master equation in the Lindblad form, according to the scenario just described, we take as a ground the second-order contribution to the evolution of the reduced phonon density operator $\rho_{ph} = \text{Tr}_{SaS} \rho$ in the time convolutionless approximation [27],

$$\frac{d\rho_{ph}}{dt} = -\lambda^2 \int_{t_i}^t du \text{Tr}_{SaS} \left\{ \left[ \hat{H}_I(t), \left[ \hat{H}_I(u), \rho_{ph}(t) \otimes \rho_{SaS} \right] \right] \right\}, \quad (10)$$

where $\rho_{SaS}$ is the density operator of the $SaS$ field. The constant $\lambda$ stands for the strength of the interaction that in our case is represented by the couplings $\alpha_{H(V)g}$. In order to derive the final equation, we will assume that these couplings follow two conditions:

$$\alpha_{H(V)g}(\omega) \ll \omega \quad \text{and} \quad |g(\omega = \omega_L \mp \nu)|^2 \sim g_0^2. \quad (11)$$

Signs $(-)$ and $(+)$ correspond to $S$ and $aS$ events, respectively. The first condition implies the weak coupling regime which is fully justified in our procedure. $|\alpha * g|^2 \sim 10^4\text{Hz}$ is proportional to the count of Stokes photons and, therefore, much smaller than the optical frequency of the fields at $\omega \sim 5 \times 10^{14}\text{Hz}$, which is of the order of the correlation time of our photonic reservoirs. The second condition means that the response of the material (|$g(\omega)$|) is basically flat in the range of frequencies involved in the experiment, which is valid when considering materials with electronic gap much higher then the excitation energies involved, such as in diamond. With no loss of generality, we will approximate it by a Gaussian function

$$|g(\omega)|^2 = g_0^2 \text{e}^{-\frac{(\omega - \omega_L)^2}{\delta^2}}, \quad (12)$$

such that $\delta \omega$ is taken much greater than all the physical parameters involved in the process. Finally, each pulse
is still well resolved in frequency, $1/\Delta t \ll \omega_L$. When put together, these conditions allow us to derive a master equation governing the phonon population distribution as a result of the interaction with the $SaS$ field. Assuming the experimentally verified equal intensity for the pump and probe pulses, $\alpha_h^2 = \alpha_v^2 = \alpha_0^2$, the contribution of the Stokes and anti-Stokes reservoirs for the dynamics of the phonons reads (see the Appendix for details):

$$\frac{dp_{ph}}{dt} = 2\pi (\alpha_0 \rho_{ph})^2 \left[ e^{-2\left(\frac{\omega_c - \omega_h}{\Delta t}\right)^2} + e^{-2\left(\frac{\omega_c - \omega_v}{\Delta t}\right)^2} \right] \times [2c^2 \rho_{ph} c + 2c \rho_{ph} c^* - \{c^\dagger, c^\dagger \rho_{ph} \}], \quad (13)$$

where $\{A, B\} = AB + BA$. The overall phononic evolution is obtained by adding the dissipative Lindblad term, in the form of Eq. (9), to the right hand side of Eq. (13). This extra term accounts for the dissipation due to other phonons of the material, as previously mentioned.

III. RESULTS

A. Description of the analyzed data

In Ref. [13] the authors used two delayed pulse beams to produce correlated Stokes and anti-Stokes photons pairs by real and virtual processes in a diamond sample. First, they investigated the polarization dependence of the $SaS$ process realizing that both $S$ and $aS$ photons carry majorly the same polarization of the excitation pulse. Then, they designed and performed time delayed cross-correlated pump-probe photon detections of $SaS$ pairs. In each run, a 76 MHz sequence of two pulses of orthogonal polarization, $H$ and $V$, were sent to the sample, each pulse centered at $\omega_L = 632.8\text{ nm}$ and of Gaussian shape with $0.40 \text{ ps FWHM}$. A polarization dependent delaying line placed before the sample established a switchable time separation $\delta \tau$ between the $H$ pump pulse and the $V$ probe pulse ranging from $-2$ to $+13 \text{ ps}$. A dichroic mirror and polarizers were placed before the photon detectors to guarantee the collection of Stokes photons of $H$ polarization and anti-Stokes photons of $V$ polarization.

The detections were made at two different pairs of frequencies, $\omega_A$ and $\omega_B$. First, photons were detected at the Raman resonance peaks with detectors placed at $\omega_A = \omega_S = \omega_L - \nu$ and $\omega_B = \omega_{aS} = \omega_L + \nu$. At these frequencies, the pair generation process is dominated by real $SaS$. Then, the detection setup was adjusted to collect pairs at displaced frequencies $\omega_A = \omega_S + \Delta$, $\omega_B = \omega_{aS} - \Delta$, where $\Delta < \nu$ and the process is dominated by virtual $SaS$. [22]

In each case, they measured the $SaS$ scattering intensity, i.e. the number of pair coincidence photon counts or, equivalently, the pairs of correlated photons detected simultaneously, by varying the time delay $\delta \tau$ between the $H$ pump pulse and the $V$ probe pulse. It was observed that the production rate of real $SaS$ pairs decreases with the decay of the phonon population generated by the Stokes process. The measured lifetime of the phonon population was around $2.8 \text{ ps}$, in agreement with results of other experiments. In contrast, in the virtual process, $SaS$ pair production occurred primarily when the two laser pulses overlapped, indicating that it happened faster than the duration of a single pulse.

B. Data analysis

In Fig. 1 we plot the experimental data from Ref. [13] and the theoretical curves obtained by solving Eq. (8) and calculating the normalised probability $P_{N_{SaS}}(\delta \tau)$ of finding a Stokes photon of polarization $H$ and an anti-Stokes photon of polarization $V$, at the respective detectors frequencies. The corresponding results for real and virtual process are represented by the dashed–red lines in Figs. 1(a) and 1(b), respectively. The distribution is plot as a function of the delay $\delta \tau$ between pump and probe pulses, for values within the interval between $-2.0 \text{ ps}$ and $12.0 \text{ ps}$, and it is given by

$$P_{N_{SaS}}(\delta \tau) = P_{ph}(\delta \tau) + CP_{max}, \quad (14)$$

where the constant $C$ refers to the experimental uncertainty caused by the production of pairs by a single laser pulse, and $P_{max}$ is the maximum value achieved by the probability $P_{SaS}(\delta \tau)$ to create a couple of $SaS$ photons by the action of the two pulses, as it was already discussed.

Both theoretical curves are calculated using the parameters obtained in the experiment, both for the pulses and the lifetime of the phonon. Notice that they fit very well the experimental data both for real and virtual pairs. Also note that the theory correctly predicts that at the Raman peaks (resonance), real pairs dominate and the probability of finding a pair depends on the decay of the phonon, whereas out of resonance the pairs are created only when the two pulses coincide, which is consistent with the formation of photonic Cooper pairs (PCPs), also observed in [8], via the exchange of virtual phonons.

In Fig. 1(a) we also plotted the theoretical curve for the phonon population, dashed-blue line, obtained by solving eq. (13). As in the previous case, the curve represents a normalized quantity:

$$P_{N_{SaS}}(\delta \tau) = \frac{P_{ph}(\delta \tau)}{P_{ph_{max}}}, \quad (15)$$

where $P_{ph}(\delta \tau)$ is the probability to create a unique phonon in the entire process, while $P_{ph_{max}}$ is the maximum value for $P_{ph}(\delta \tau)$.

The parameters used for the pulses, as well as the phonon natural lifetime are the same as in the dashed-red curve. The result confirms the accuracy of the phenomenological model used in [13] for the probability of generating real $SaS$ pairs, and reinforces the validity of the hypothesis used to derive eq. (13). At the Raman
peaks, the pair formation is indeed dominated by real processes and depends basically on a second pump photon combining with the phonon created in the Stokes scattering to create the correlated anti-Stokes component of the pair.

IV. CONCLUSIONS

In this paper we have introduced an effective Hamiltonian to describe the correlated $SaS$ photon pair production in Raman scattering by both real and virtual processes. In particular, we considered the cases when the material is shined by two laser pulses of orthogonal polarizations with a time-delay one from the other. We have also derived a non-unitary dynamics for the vibration of the material considering the Stokes and anti-Stokes fields as external pumping and dissipative reservoirs. We tested the validity of our model by comparing the theoretical results with the experimental data measured in Ref. [13]. The Hamiltonian model confirms the experimental data in both regimes (real and virtual pairs). In particular, our model predicts correctly that, at the Raman resonance peaks, the process is dominated by the lifetime of the phonon, therefore by real $SaS$ pairs, whereas out of the resonance peaks, it is centered at zero delay and defined basically by the inverse linewidth of the pump and probe pulses, hence, dominated by virtual $SaS$ pairs. Furthermore, the model for the dynamics of the phonon distribution also adequately describes the real $SaS$ data. This second result demonstrates that the phenomenological model used in [13] is sound and correctly captures the essence of the production of pairs at the Raman resonance peaks and under the experimental conditions used therein.

V. ACKNOWLEDGMENTS

We thank Filomeno S. de Aguiar Júnior for providing us with the experimental data. This work was supported by FAPERJ Projects No. E-26/202.290/2018 and No. E-26/202.576/2019 and by CNPq Projects No. 302872/2019-1, 307481/2013-1, 429165/2018-8 and No. INCT-IQ 465469/2014-0.

VI. APPENDIX

Here we derive the master equation in the Lindblad form of the reduced phonon density operator, eq. (13). To this aim, we consider the second order contribution to the dynamics of an open system in the time convolutionless approximation, which it defined by eq. (10). Hence, for eqs. (6)-(7), introducing Eqs. (16a)-(16b) below explicitly into Eq. (10),

$$\text{Tr}_{SaS} \left\{ b_{S_{H(V)}}(\omega_1) b_{S_{H(V)}}^\dagger (\omega_2) \rho_{SaS} \right\} = \delta(\omega_1 - \omega_2), \quad (16a)$$

$$\text{Tr}_{SaS} \left\{ b_{aS_{H(V)}}(\sigma_1) b_{aS_{H(V)}}^\dagger (\sigma_2) \rho_{SaS} \right\} = \delta(\sigma_1 - \sigma_2), \quad (16b)$$

and considering the following relations,

$$\text{Tr}_{SaS} \left\{ b_{S_i}(\omega_1) b_{S_j}(\omega_2) \rho_{SaS} \right\} =$$

$$\text{Tr}_{SaS} \left\{ b_{S_i}^\dagger (\omega_1) b_{S_j}^\dagger (\omega_2) \rho_{SaS} \right\} = 0, \quad (16b)$$

$$\text{Tr}_{SaS} \left\{ b_{aS_i}(\sigma_1) b_{aS_j}(\sigma_2) \rho_{SaS} \right\} =$$

$$\text{Tr}_{SaS} \left\{ b_{aS_i}^\dagger (\sigma_1) b_{aS_j}^\dagger (\sigma_2) \rho_{SaS} \right\} = 0, \quad (16b)$$

$$\text{Tr}_{SaS} \left\{ b_{S_i}(\omega) b_{aS_j}(\sigma) \rho_{SaS} \right\} =$$

$$\text{Tr}_{SaS} \left\{ b_{aS_i}(\sigma) b_{S_j}(\omega) \rho_{SaS} \right\} = 0, \quad (16c)$$

$$\text{Tr}_{SaS} \left\{ b_{S_i}^\dagger (\omega) b_{aS_j}(\sigma) \rho_{SaS} \right\} =$$

$$\text{Tr}_{SaS} \left\{ b_{aS_i}(\sigma) b_{S_j}^\dagger (\omega) \rho_{SaS} \right\} = 0, \quad (16d)$$
for \(i, j \in \{H, V\}\), we get

\[
\frac{d\rho_{ph}}{dt} = -\int_{t_1}^{t} du \left[ f_H(t-t_0)f_H(u-t_0) + f_V(t-t_1)f_V(u-t_1) \right] \times \\
\left[ \int_{0}^{\infty} d\omega |g(\omega)|^2 e^{i\Delta_1(u-t_0)} c_1^\dagger \rho_{ph} + \int_{0}^{\infty} d\sigma |g(\sigma)|^2 e^{i\Delta_2(u-t_1)} c_1^\dagger \rho_{ph} + \int_{0}^{\infty} d\omega |g(\omega)|^2 e^{-i\Delta_1(u-t_0)} \rho_{ph} c_1^\dagger \rho_{ph} \right] \\
+ \int_{0}^{\infty} d\sigma |g(\sigma)|^2 e^{-i\Delta_2(u-t_1)} \rho_{ph} c_1 c^\dagger \rho_{ph} - \int_{0}^{\infty} d\omega |g(\omega)|^2 e^{-i\Delta_1(u-t_0)} \rho_{ph} c c^\dagger \rho_{ph} + \int_{0}^{\infty} d\sigma |g(\sigma)|^2 e^{i\Delta_2(u-t_1)} \rho_{ph} c^\dagger \rho_{ph} - \int_{0}^{\infty} d\omega |g(\omega)|^2 e^{i\Delta_1(u-t_0)} \rho_{ph} c c^\dagger \rho_{ph} \right].
\]

(17)

The function \(f_j(t-t_j)\) in the integrand is given by

\[
\begin{align*}
  f_j(t-t_j) &= \alpha_j e^{\left(-\frac{(t-t_j)}{\tau}\right)^2}, \\
  \end{align*}
\]

(18)
such that, after removing the parenthesis in the integrand of (17), we have integrals of the following type,

\[
I = \int_{t_1}^{t} du f_j(u-t_j) \int_{0}^{\infty} d\mu |g(\mu)|^2 e^{\pm i\Delta_k(u-t)},
\]

(19)

where the index \(j\) replaces the \(H\) and \(V\) ones, and \(t_j\) stands for the time where the maximum of the respective Gaussian occurs, while \(\Delta_k = \Delta_{1,2}\). Now, since the integrand in the time integral decrease fairly quickly for times above and below of \(t_j\) we extend the lower and upper integration limits to \(-\infty\) and \(+\infty\), respectively. This fact together with the assumptions established by Eqs. (16a,16b) determine the validity of the Markov approximation in our approach. Then, we can write,

\[
I = \alpha_a \int_{0}^{\infty} d\mu |g(\mu)|^2 \int_{-\infty}^{\infty} du e^{-(\frac{u-t_j}{\tau})^2} e^{\pm i\Delta_k(u-t)} \\
= \alpha_a \sqrt{\pi} \Delta t \int_{0}^{\infty} d\mu |g(\mu)|^2 e^{-(\frac{\Delta_k}{\tau A})^2} e^{\pm i\Delta_k(t-t_0)}. \]

(20)

To perform the integral in frequency we assume the response of the material \(|g(\mu)|\) can be approximated by eq. (12) as discussed before. In view of \(\omega_L >> 0\) we can again extend the lower integration, in (20), to minus infinite, so the integral \(I\) reads

\[
I = \alpha_a g_0^2 \sqrt{\pi} \Delta t \left[ \int_{-\infty}^{\infty} du \, \frac{(\frac{A^2}{\omega_L})^2}{\omega_L^2} e^{-(\frac{\Delta_k}{\tau A})^2} e^{\pm i\Delta_k(t-t_0)} \right] \\
= \alpha a g_0^2 \sqrt{\pi} \Delta t \left[ e^{-(\frac{A^2}{\omega_L})^2} e^{-(\frac{\Delta_k}{\tau A})^2} e^{\pm i\Delta_k(t-t_0)} \int_{-\infty}^{\infty} du \, e^{-A^2 \mu^2} e^{B \mu + i \gamma(t-t_0)\mu} \right] \\
= \alpha a g_0^2 \sqrt{\pi} \Delta t \left[ e^{-(\frac{A^2}{\omega_L})^2} e^{-(\frac{\Delta_k}{\tau A})^2} e^{\pm i\Delta_k(t-t_0)} \right] \left[ \frac{\sqrt{\pi} e^{\frac{B\gamma(t-t_0)}{4\tau A^2}}}{A} \right]^2,
\]

(21)

with

\[
\begin{align*}
A^2 &= \left(\frac{\Delta_k}{\tau A}\right)^2 + \frac{1}{\delta \mu^2}, \\
B &= \frac{2\omega_L}{\delta \mu^2} - \frac{\delta \Delta_k^2}{2}, \\
s &= \nu - \omega_L \to S (aS).
\end{align*}
\]

(22)

Taking \(\delta \mu^2\) much greater than all the physical parameters concerning to (21), it yields

\[
I = 2\pi \alpha a g_0^2 e^{-(\frac{\Delta_k}{2\tau A})^2}.
\]

(23)

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