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Collective two-particle resonances induced by photon entanglement

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Abstract

An assembly of non interacting atoms may become correlated upon interaction with entangled photons, and certain elements of their joint density matrix can then show collective resonances. We explore experimental signatures of these resonances in the nonlinear response of a pair of two-level atoms. We find that these resonances are canceled out in stimulated signals such as pump-probe and two photon absorption due to destructive interference of two-photon-absorption and emission pathways in the joint two-particle space. However, they may be observed in photon statistics (Hanbury-Brown Twiss) measurements through the attenuation of two-time intensity correlations.

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I. INTRODUCTION

Two photon absorption of entangled photon pairs has been in the focus of extensive current research. The linear (rather than quadratic) scaling of the signal with the incident entangled photon generating laser intensity is promising for imaging applications, since it allows to use much lower intensities[1–3], and avoid damage to the sample. Sources of non classical light with entangled photons are currently widely used in quantum information processing and secure communication.

Since the interaction with entangled photons can induce correlations and entanglement of otherwise uncorrelated atoms, it is natural to expect new collective many-particle resonances in the nonlinear response [18].

The standard calculation of the non linear response to classical light assumes that the matter is made up of N non interacting systems (atoms or molecules) in the active zone. The individual nonlinear susceptibilities or response functions of these atoms are additive; For identical atoms it is sufficient to calculate the susceptibility of a single atom and multiply it by N. The nonlinear response becomes then a single body problem and no cooperative resonances are expected. It is not obvious how to rationalize the N scaling for non interacting atoms had we chosen to perform the calculation in the many body space. Massive cancellations of most light matter pathways recover in the end the final N signal scaling [4].

When the atoms are coupled, the calculation needs to be done in their direct-product many-body space whose size grows exponentially with N ($\sim n^N$ dimensions for n-level atoms). For measurements with weak optical fields, only a smaller, power-law scaling, subspace with few excitations is needed, e. g. the third order response only depends on $\sim N$ single exciton states and $\sim N(N-1)/2$ two exciton states. Multiexcitonic states show up in the response of molecular aggregates such as photosynthetic complexes [5].

The interatomic coupling can be induced by the exchange of virtual photons leading to dipole-dipole and cooperative spontaneous emission, superradiance [6]. In an insightful article [7], which inspired other work [8, 9], it was argued, that using time ordered entangled photon pairs, two-body two-photon resonances, where two particles are excited simultaneously, can be observed in two photon absorption. This implies that the nonlinear response is no longer additive and does not scale as N. Such cooperativity is not possible with clas-

sical or coherent light field. Arguments were made that these are induced in two photon absorption by the manipulation of the interference among pathways.

One consequence of this prediction is that the fluorescence from one atom can be enhanced by the presence of a second atom, even if they do not interact. This could be an interesting demonstration of quantum nonlocality and the EPR paradox. In this paper we use a superoperator formalism [10] to compute the nonlinear response to entangled light and examine these arguments more closely. We investigate the destructive interference of pathways for a pair of uncoupled two level atoms and analyze in which optical observables the two photon resonances could be detected. We neglect direct interactions through the exchange of photons, where cooperative effects are well known to occur, and only consider uncoupled atoms, as was done in [7].

We find that pump probe signals contain no signature of particle correlations. They remain additive $\sim N$ scaling. Two particle resonances then cancel out by destructive interference of pathways in the two body space and collective two photon absorption resonances are absent, as in the case of classical light. However, Hanbury-Brown Twiss correlations [11] do show signatures of cooperativity.

In Section II, we discuss the matter correlation induced by entangled photons, then in Section III, we show that the two particle resonances in pump probe signals interfere destructively. Finally in Section IV, we show how they can be observed through attenuation of the photon-photon correlations.

II. CORRELATIONS INDUCED IN MATTER BY ENTANGLED PHOTONS

We consider two non-interacting atoms A and B coupled to the radiation field and described by the Hamiltonian:

$$H = H_A + H_B + H_F + H^A_{int} + H^B_{int}, \tag{1}$$

$$H^A_{int} = \tilde{V}_A \tilde{E}, \qquad H^B_{int} = \tilde{V}_B \tilde{E}. \tag{2}$$

Here H_A and H_B are the matter Hamiltonians and $\tilde{V}_A$ and $\tilde{V}_B$ are the dipole operators of atoms A and B, H_F is the field Hamiltonian and $\tilde{E}$ is the total optical electric field operator.

We assume that the density matrix of the entire system is initially in a factorisable state:

$$\rho(t_0) = \rho_{A,0} \otimes \rho_{B,0} \otimes \rho_{ph,0}. \tag{3}$$

In the following we will use the interaction picture, where all time dependent operators evolve with $H_0 = H_F + H_A + H_B$. The bookkeeping is greatly simplified by formulating the problem using superoperators: For an arbitrary ordinary operator O, we define $O_L\rho = O\rho$ (left action) and $O_R\rho = \rho O$ (right action). We further define their linear combinations $O_- = O_L - O_R$ and $O_+ = \frac{1}{2}(O_L + O_R)$ [19]. The time dependent density matrix is then given by:

$$\rho(t) = T\exp(-\frac{\imath}{\hbar}\int_{t_0}^{t} H^A_{int,-}(\tau)\mathrm{d}\tau - \frac{\imath}{\hbar}\int_{t_0}^{t} H^B_{int,-}(\tau)\mathrm{d}\tau)\rho_{0,A}\rho_{0,B}\rho_{ph,0}. \tag{4}$$

Here T is the time ordering operator, which when acting on products of superoperators, it reorders them with increasing time arguments from right to left.

If the radiation field is classical then the matter density matrix factorizes and atoms A and B remain uncorrelated at all times[12]:

$$\rho(t) = \rho_A(t)\rho_B(t) \tag{5}$$

with:

$$\rho_A(t) = T\exp(-\frac{\imath}{\hbar}\int_{t_0}^{t} H^A_{int,-}(\tau)\mathrm{d}\tau)\rho_{0,A}, \tag{6}$$

$$\rho_B(t) = T\exp(-\frac{\imath}{\hbar}\int_{t_0}^{t} H^B_{int,-}(\tau)\mathrm{d}\tau)\rho_{0,B}. \tag{7}$$

This result remains valid for quantum fields, as long as all relevant field modes are in a coherent state, and cooperative spontaneous emission is neglected and therefore behave classically [10, 13].

For a quantum field we substitute Eq. (2) in Eq. (4) and obtain:

$$\begin{aligned}\rho(t) \;=\; T\exp(&-\frac{\imath}{\hbar}\int_{t_0}^{t} \tilde{V}^A_L(\tau)\tilde{E}_L(\tau) - \frac{\imath}{\hbar}\int_{t_0}^{t} \tilde{V}^B_L(\tau)\tilde{E}_L(\tau)\\ &+\frac{\imath}{\hbar}\int_{t_0}^{t} \tilde{V}^A_R(\tau)\tilde{E}_R(\tau) + \frac{\imath}{\hbar}\int_{t_0}^{t} \tilde{V}^B_R(\tau)\tilde{E}_R(\tau))\rho_{0,A}\rho_{0,B}\rho_{ph,0}.\end{aligned} \tag{8}$$

We define the reduced matter density matrix in the joint space $w := \mathrm{tr}_{ph}(\rho)$. Upon expanding Eq. (8) order by order in the field operators and tracing over the field modes, we obtain the formal expansion:

$$\begin{aligned}w(t) \;=\; \sum_\nu \int_{t_0}^{t}\mathrm{d}\tau_1 \ldots \int_{t_0}^{t}\mathrm{d}\tau_{n_\nu} \int_{t_0}^{t}\mathrm{d}\tau'_1 \ldots \int_{t_0}^{t}\mathrm{d}\tau'_{m_\nu} \rho^\nu_A(\tau_1 \ldots \tau_{n_\nu})\rho^\nu_B(\tau'_1 \ldots \tau'_{m_\nu})\\ F_\nu(\tau_1 \ldots \tau_{n_\nu}, \tau'_1 \ldots \tau'_{m_\nu}).\end{aligned} \tag{9}$$

where ν is summed over all possible pathways. Pathway ν has n_ν $\tilde{V}^A$ interactions and m_ν $\tilde{V}^B$ interactions. ρ_A^ν (ρ_B^ν) are time ordered products of system A (system B) operators and $F_\nu(\tau_1 \ldots \tau_{n_\nu}, \tau'_1 \ldots \tau'_{m_\nu})$ are time ordered field correction functions. In each term of this perturbative order by order calculation all the correlation functions are factorized between the three spaces. The factorization Eq. (5) now no longer holds and atoms A and B may become correlated or even entangled. We shall apply Eq. (9) in the following. Note that pathways with $n_\nu = 0$ or $m_\nu = 0$ are *single body pathways*, where all interactions occur either with system A or with B. Our interest is in the *two body pathways*, that can contribute to collective response, where both n_ν and m_ν are finite.

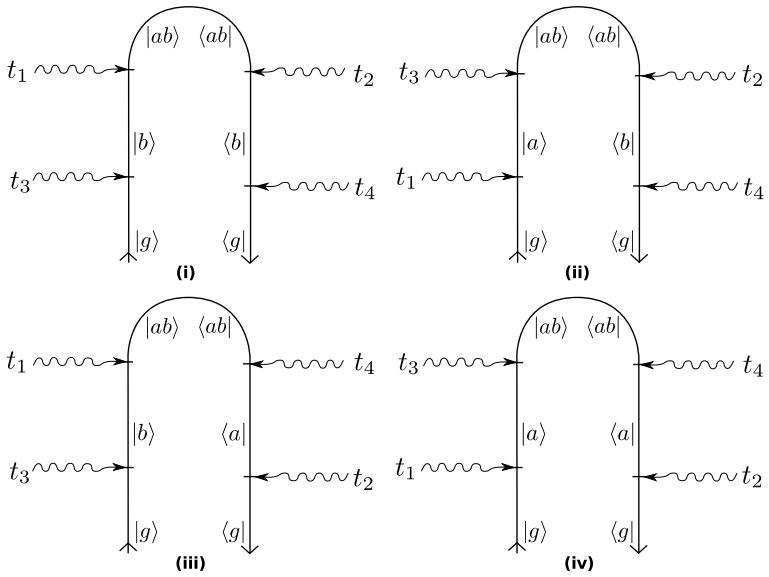

Figure 1: The four unrestricted open-loop diagrams, which represent $P_{ab}(t)$. For rules see Ref. 14. These diagrams correspond respectively to the integrands of the four terms in Eq. (A1).

A. Fourth order two body contributions to the density matrix

We assume that systems A and B are two-level atoms. The joint system has three states: state $|a\rangle$ where system A is excited and system B is in ground state, $|b\rangle$ where system B is excited and system A is in ground state and the state $|ab\rangle$ where both systems are excited. The material Hamiltonian $H_{0,el}$ expanded in this basis thus reads:

$$H_A + H_B = \hbar\varepsilon_a|a\rangle\langle a| + \hbar\varepsilon_b|b\rangle\langle b| + \hbar(\varepsilon_a + \varepsilon_b)|ab\rangle\langle ab|. \tag{10}$$

Hereafter we shall treat the matter-light interaction in the rotating wave approximation (RWA). To that end, we partition $\tilde{E}$ and $\tilde{V}$ into positive (E, V) and negative frequency ($E^\dagger$, $V^\dagger$) components $\tilde{E} = E + E^\dagger$ and $\tilde{V} = V_A + V_B + V_A^\dagger + V_B^\dagger$ with:

$$\begin{aligned} V_A &= \mu_a(|g\rangle\langle a| + |b\rangle\langle ab|), \\ V_B &= \mu_b(|g\rangle\langle b| + |a\rangle\langle ab|), \\ H_{int} &= V_A E^\dagger + V_B E^\dagger + V_A^\dagger E + V_B^\dagger E. \end{aligned} \tag{11}$$

We first calculate the population of the $|ab\rangle$ state $P_{ab}(t) = \mathrm{tr}(|ab\rangle\langle ab|\rho(t))$ to lowest order $\mu_A^2\mu_B^2$ of two body contributions. It can be represented by the unrestricted loop diagrams shown in Fig. 1 (see [14] for a rules and definitions).

The four terms corresponding to the four diagrams are given in Eq. (A1). They can be combined to a single term with non ordered time variables.

$$\begin{aligned} P_{ab}(t) &= \left(-\frac{\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t} \mathrm{d}t_4 \langle g_A|V_A(t_2)V_A^\dagger(t_1)|g_A\rangle\langle g_B|V_B(t_4)V_B^\dagger(t_3)|g_B\rangle \\ &\quad \langle E^\dagger(t_4)E^\dagger(t_2)E(t_3)E(t_1)\rangle. \end{aligned} \tag{12}$$

Since systems A and B are uncoupled, the relative time orderings of interactions with systems A and B is immaterial: A prior interaction of system A does not change system B at all and vice versa. This is why we could combine the four diagrams to yield a single term with non time ordered time variables.

We note that if the system starts in a pure state $|\psi\rangle$, we can express $P_{ab}(t)$ as transition matrix between the initial state $|\psi\rangle$ and the final state $|\psi'\rangle$ as:

$$\begin{aligned} P_{ab}(t) &= \left| \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \mu_A\mu_B e^{-\imath\varepsilon_a t_1 - \imath\varepsilon_b t_2} \langle\psi|E(t_2)E(t_1)|\psi'\rangle \right|^2 \\ &:= |T_{ab}(t)|^2 \end{aligned} \tag{13}$$

with $V_A^\dagger(t_1) = e^{\imath\varepsilon_a t_2}\mu_A(|a\rangle\langle g| + |ab\rangle\langle b|)$.

We first evaluate Eq. (12) using a classical field composed of two modes ω_α and ω_β, which is switched on at $t = t_0$:

$$\tilde{E}(t) = \theta(t - t_0)(E_\alpha e^{\imath\omega_\alpha t} + E_\beta e^{\imath\omega_\beta t}) + c.c.. \tag{14}$$

$T_{ab}(t)$ is then given by:

$$\begin{aligned} T_{ab}(t) &= \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t} \mathrm{d}t_4 E^{\dagger}(t_4) E^{\dagger}(t_2) e^{-\imath E_a t_2 - \imath E_b t_4} \\ &= -\frac{A_{\alpha b}(t) A_{\alpha a}(t)}{(\varepsilon_b - \omega_\alpha - \imath\gamma)(\varepsilon_a - \omega_\alpha - \imath\gamma)} - \frac{A_{\alpha b}(t) A_{\beta a}(t)}{(\varepsilon_b - \omega_\alpha - \imath\gamma)(\varepsilon_a - \omega_\beta - \imath\gamma)} \\ &\quad -\frac{A_{\beta b}(t) A_{\alpha a}(t)}{(\varepsilon_b - \omega_\beta - \imath\gamma)(\varepsilon_a - \omega_\alpha - \imath\gamma)} - \frac{A_{\beta b}(t) A_{\beta a}(t)}{(\varepsilon_b - \omega_\beta - \imath\gamma)(\varepsilon_a - \omega_\beta - \imath\gamma)} \end{aligned} \tag{15}$$

with $\gamma \to 0$ and

$$A_{\nu m}(t) = E_\nu (e^{\imath(\omega_\nu - \varepsilon_m)t_0 - \gamma t_0} - e^{\imath(\omega_\nu - \varepsilon_m)t - \gamma t}). \tag{16}$$

We can further recast this as a product of probabilities, as expected from Eq. (5) for the classical case:

$$P_{ab}(t) = \left| \frac{\imath A_{\alpha a}(t)}{(\varepsilon_a - \omega_\alpha - \imath\gamma)} + \frac{\imath A_{\beta a}(t)}{(\varepsilon_a - \omega_\beta - \imath\gamma)} \right|^2 \left| \frac{\imath A_{\alpha b}(t)}{(\varepsilon_b - \omega_\alpha - \imath\gamma)} + \frac{\imath A_{\beta b}(t)}{(\varepsilon_b - \omega_\beta - \imath\gamma)} \right|^2. \tag{17}$$

This expression contains only single particle resonances $\omega_a - \omega_\alpha$, $\omega_b - \omega_\beta$ and no two photon resonances $\omega_a + \omega_b - \omega_\alpha - \omega_\beta$ (cf. [12]).

We next consider a field made of entangled photon pairs of a cascade state $|\psi_c\rangle$ as used in [7] and described by the wavefunction:

$$\begin{aligned} |\psi_c\rangle &= \sum_{p,q} \phi_{p,q} |1_p, 1_q\rangle, \\ \phi_{p,q} &= \frac{g_{p\alpha} g_{q\beta} \exp[\imath(\boldsymbol{p} + \boldsymbol{q}) \cdot \boldsymbol{r}_R]}{(\omega_p + \omega_q - \omega_\alpha - \omega_\beta + \imath\gamma_\alpha)(\omega_q - \omega_\beta + \imath\gamma_\beta)}. \end{aligned} \tag{18}$$

Where γ_α is the lifetime of the upper level of the three level cascade and γ_β is the lifetime of the intermediate state. p and q are the wavevectors of different modes in vacuum and $g_{p\alpha}$ are coupling constants. ω_α is the transition frequency from the highest to the intermediate state and ω_β is the transition frequency from the intermediate state to the ground state. The two photon frequency $\omega_p + \omega_q$ is distributed around $\omega_\alpha + \omega_\beta$ with a narrow width of γ_α the lifetime of the upper level, whereas the single photon frequencies ω_q ω_p are distributed around ω_β (ω_α) with a width of γ_β (γ_α) the lifetime of the intermediate (highest) level. Maximum entanglement occurs for $\gamma_\beta \gg \gamma_\alpha$. Using Eq. (18) we have:

$$\begin{aligned} \langle \psi_c | E(t_2) E(t_1) | vac \rangle &= A\theta(t_1 - t_R)\theta(t_2 - t_1) e^{(\imath\omega_\beta - \gamma_\beta)(t_2 - t_R)} e^{(\imath\omega_\alpha - \gamma_\alpha)(t_1 - t_R)} \\ &\quad + A\theta(t_2 - t_R)\theta(t_1 - t_2) e^{(\imath\omega_\beta - \gamma_\beta)(t_1 - t_R)} e^{(\imath\omega_\alpha - \gamma_\alpha)(t_2 - t_R)} \end{aligned} \tag{19}$$

Here, $\theta(t_2-t_1)$ and $\theta(t_1-t_2)$ assure that photons emitted around ω_α come first followed by ω_β. We assume that the A and B atoms have the same distance from the cascade source, so that t_R is the time retardation (with $t_R = |\boldsymbol{r}_R|/c$).

$$\begin{aligned} T_{ab}(t) &= \mu_A\mu_B A \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t} \mathrm{d}t_4 \langle\psi_c|E^\dagger(t_4)E^\dagger(t_2)|vac\rangle e^{-\imath\varepsilon_a t_2 - \imath\varepsilon_b t_4} \\ &= \frac{A_{b\alpha,a\beta}(t)}{(\varepsilon_b-\omega_\alpha-\imath\gamma_\alpha)(\varepsilon_a-\omega_\beta)-\imath\gamma_\beta} \\ &\quad + \frac{A_{a\alpha,b\beta}(t)}{(\varepsilon_a-\omega_\alpha-\imath\gamma_\alpha)(\varepsilon_b-\omega_\beta-\imath\gamma_\beta)} \\ &\quad + \frac{A_{TPA}(t)(\varepsilon_a+\varepsilon_b-2\omega_\beta-\imath 2\gamma_\beta)}{(\varepsilon_a-\omega_\beta-\imath\gamma_\beta)(\varepsilon_b-\omega_\beta-\imath\gamma_\beta)(\varepsilon_a+\varepsilon_b-\omega_\beta-\omega_\alpha-\imath\gamma_\alpha-\imath\gamma_\beta)} \end{aligned} \tag{20}$$

with

$$A_{n\nu,m\mu}(t) = \mu_A\mu_B A(e^{\imath\omega_{nu}(t-t_R)-\gamma_\nu(t-t_R)} - e^{-\imath\varepsilon_m t_R - \imath\varepsilon_n t_R}), \tag{21}$$

$$A_{TPA}(t) = \mu_A\mu_B A(e^{-\imath\varepsilon_a t_R - \imath\varepsilon_b t_R} - e^{-\imath(\varepsilon_a+\varepsilon_b)t + \imath(\omega_\alpha-\omega_\beta-\gamma_\alpha-\gamma_\beta)(t-t_R)}). \tag{22}$$

The first two terms in Eq. (20) represent single-particle-resonances, where the two systems are excited individually. They differ only in the time ordering in which the two photons excite the two systems, so in the first term the interaction with the atom A comes first and atom B is excited first. The third term represents collective two photon resonances $\varepsilon_a+\varepsilon_b-\omega_\beta-\omega_\alpha$. This resonance disappears, if $\omega_\alpha=\omega_\beta$ and $\gamma_\alpha=\gamma_\beta$, since then $(\varepsilon_a+\varepsilon_b-\omega_\beta-\omega_\alpha-\imath\gamma_\alpha-\imath\gamma_\beta)$ and $\varepsilon_a+\varepsilon_b-2\omega_\beta-\imath 2\gamma_\beta$ cancel. In that case the two photon cannot be distinguished, since both parameters ω and γ are the same. Therefore the entangled photon pair does not include a distinguishable time ordering (no which-way information) like in the other cases. This causes are full destructive cancellation, since it contains no information about the time ordering of the photons like in the classical case. These arguments were made in [7].

Comparing Eq. (15) and Eq. (20), we see that two photon resonances are induced by the lack of time ordering in the photonic field. This is a second kind of a interference effect, the first interference, which eliminates one particle observables, was based on the lack of time ordering of the absorption of the two systems, while this interference effect originally described in [7] is based on a lack of time ordering of the two photons. Only the single body single photon resonances remain.

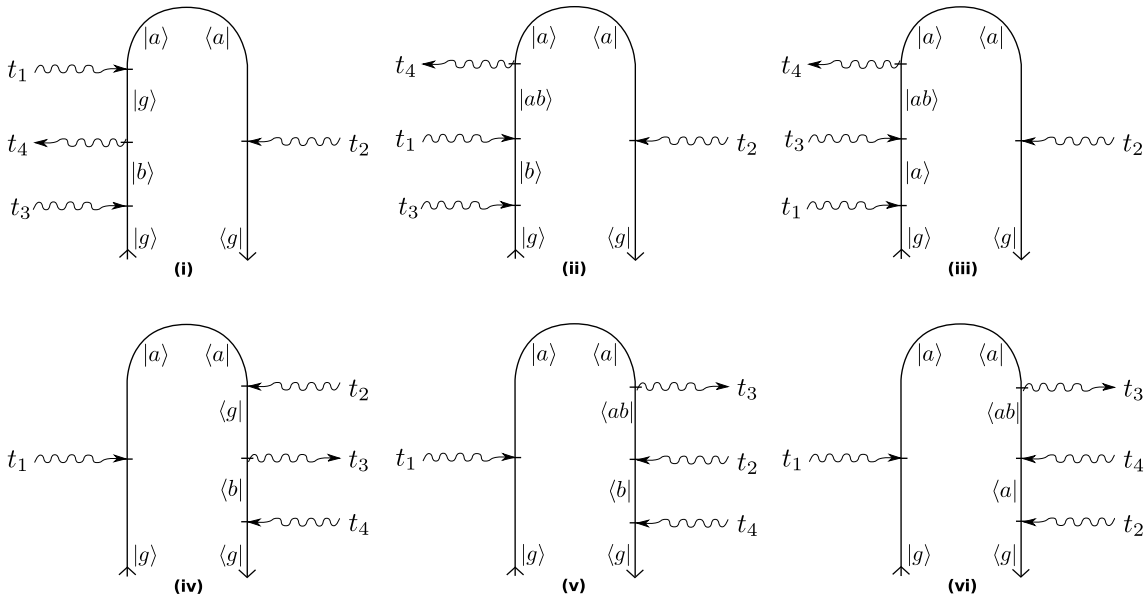

Figure 2: The six unrestricted open-loop diagrams which represent $P_a(t)$. These diagrams correspond respectively to the integrands of the six terms in Eq. (A2).

In summary, we have demonstrated that after the interaction with entangled photons the matter density matrix is no longer of a direct product form $\rho_A\rho_B$. It becomes correlated and shows collective two particle resonances.

We next turn to the excited state population of A, which is given by $P_{ab}(t)+P_a(t)$, where $P_a(t) = \mathrm{tr}(|a\rangle\langle a|\rho(t))$ (the population of the excited state of A is the sum of two terms with B either in excited or unexcited state). We shall calculate only the $\sim \mu_A^2\mu_B^2$ contributions to P_a, which are relevant to our discussion. There are of course other single body terms $\sim \mu_A^2$ and $\sim \mu_A^4$, which will be ignored. $P_a(t)$ is given by the six diagrams given in Fig, 2 and corresponding equations are given in Eq. (A2).

Diagrams (ii), (iii), (v) and (vi) contain the normally-ordered field correlation function $\langle E^\dagger(\tau_4)E^\dagger(\tau_3)E(\tau_2)E(\tau_1)\rangle$, that entered in P_{ab} (Eq. (12). Here, two photons are first absorbed and then emitted. Both absorptions are caused by the incident photons and are therefore stimulated by the external light source. These four terms will be denoted two photon absorption (TPA) pathways. *Note that these products are ordered along the loop but not in real time.* The other two diagrams ((i) and (iv)) contain the $\langle E^\dagger(t_2)E(t_3)E^\dagger(t_4)E(t_1)\rangle$ correlation function. They represent the sequence (along the loop) absorption, emission, absorption emission, where a photon is absorbed and emitted followed by a second absorption

and emission of a photon. This can be recast as a normally ordered correlation plus a term that includes a commutator:

$$\langle E^\dagger(t_2)E(t_3)E^\dagger(t_4)E(t_1)\rangle = \langle E^\dagger(t_2)E^\dagger(t_4)E(t_3)E(t_1)\rangle + \langle E^\dagger(t_2)[E(t_3),E^\dagger(t_4)]E(t_1)\rangle \quad (23)$$

The second absorbed photon can be either from the external photon field or a spontaneously emitted photon from the atom, which absorbed the first photons. We shall therefore denote the second term a spontaneous emission pathway.

Since the commutators are c numbers, this emission and absorption does not depend on the external fields and is therefore a spontaneous process. The spontaneous emission pathways introduce a coupling between the two systems, since a photon emitted by system B can be absorbed by system A. This coupling has both real (dipole-dipole) and imaginary (superadiance) parts. These couplings will obviously result in collective signals which involve several atoms. We shall consider conditions where these couplings are weak and the spontaneous terms may be safely neglected. The spontaneous contributions, responsible for superradiance, are proportional to $\frac{\gamma}{\varepsilon_a-\varepsilon_b}$, where γ is the radiative decay rate. We assume a large frequency mismatch $\varepsilon_a - \varepsilon_b$, so that we can make this parameters small. Hereafter we neglect these contributions [15]. The question we wish to address is whether cooperative effects exist in this limit through the manipulation of the stimulated pathways.

In the case of classical or coherent fields, the two terms in Eq. (23) can be easily distinguished experimentally since the former scale quadratically in the incident light intensity, whereas the latter scale linearly. For measurements with entangled photon pairs. Both scale linearly and the distinction is less obvious.

$P_a(t)$ includes also spontaneous contributions. For them the time ordering between atoms A and B is crucial Eq.(A2), by causality since a photon can only be absorbed, if it was emitted before the absorption. If we neglect the spontaneous contributions and only include the stimulated ones, we can write it also as a single term with non time ordered variables (cf. Fig. 2 and Eq. (A2):

$$P_a(t) = -P_{ab}(t), \quad (24)$$

so that the population of the excited state of A $P_a(t) + P_{ab}(t)$ is zero and is not affected by the collective resonances. Those resonances present processes, where the state with atom B unexcited transfers to the state with an excited atom B without affecting the reduced

density matrix of A ρ^A. We thus do not expect any enhanced fluorescence from A. The two photon absorption signal vanishes.

Below, we show in an alternative way, why single particle properties are not affected by two body contributions. In Liouville space the time dependent density matrix is given by Eq. (4). We now make use of the algebraic relation of superoperators[10]:

$$H_{int,-} = E_+ V_- + E_- V_+. \tag{25}$$

Let us first assume, that the electric field operators commute and set $E_- = 0$. We then calculate the expectation value of a system A operator O_A:

$$\begin{aligned} \mathrm{tr}(O_A \rho(t)) \; = \; \mathrm{tr}(O_A T \exp\left(-\frac{\imath}{\hbar}\int_{t_0}^{t} E_+(t') V_-^A(t') \mathrm{d}t'\right) \\ \exp\left(-\frac{\imath}{\hbar}\int_{t_0}^{t} E_+(t') V_-^B(t') \mathrm{d}t'\right) \rho_{A,0}\rho_{B,0}\rho_{ph,0}). \end{aligned} \tag{26}$$

Since the trace of a commutator vanishes and since there are only V_-^B operators for system B, then all correlation functions of the form $\langle V_-^B V_-^B \cdots V_-^B \rangle = 0$. The only contributing terms are when the second exponent is expanded to the zeroth order. We thus get

$$\mathrm{tr}(O_A \rho(t)) \; = \; \mathrm{tr}_{ph}(\mathrm{tr}_A(O_A T_A \exp\left(-\frac{\imath}{\hbar}\int_{t_0}^{t} E_+(t') V_-^A(t') \mathrm{d}t'\right) \rho_{A,0})\rho_{ph,0}). \tag{27}$$

The nonlinear response function is thus additive despite the non linearity (Eq. (28)), where S_A (S_B) is given by the response of the isolated system A (B). There are no cooperative terms. The $E_- V_+$ terms in Eq. (25), which were ignored in the argument contain field commutators and are responsible for the spontaneous terms, which represent radiative transfer and were neglected in this work.

III. TWO-BODY CONTRIBUTIONS TO THE PUMP-PROBE SIGNAL CANCEL BY INTERFERENCE

In Section II, we argued based on the analysis of matter pathways, that the two photon absorption signal should show no collective two particle contributions. Here we derive the same result it by calculating the pump probe signal directly. We show that this signal contains no collective resonances. Two photon absorption is a component of the pump probe signal and thus does not show such resonances.

Pump probe signals are obtained by a superposition of the field generated in the sample with an external (local oscillator) field E_d. They are given by [10]:

$$S_{pp} = S_A + S_B, \tag{28}$$

$$S_\nu(t) = \mathrm{Im}(\mathrm{tr}(E_d^\dagger(t)V_\nu(t)\rho(t))) \quad \nu = A, B, \tag{29}$$

where E_d denotes the group of modes of the optical field, which are detected. Starting with Eq. (9), the pump probe signal of A and B has the general form:

$$\begin{aligned} S_{pp}(t) = \sum_\nu \int_{t_0}^t \mathrm{d}\tau_1 \ldots \int_{t_0}^t \mathrm{d}\tau_{n_\nu} \int_{t_0}^t \mathrm{d}\tau'_1 \ldots \int_{t_0}^t \mathrm{d}\tau'_{m_\nu} (\mathrm{tr}_A(V_A\rho_A^\nu(\tau_1 \ldots \tau_{n_\nu}))\mathrm{tr}_B(\rho_B^\nu(\tau'_1 \ldots \tau'_{m_\nu})) \\ +\mathrm{tr}_A(\rho_A^\nu(\tau_1 \ldots \tau_{n_\nu}))\mathrm{tr}_B(V_B\rho_B^\nu(\tau'_1 \ldots \tau'_{m_\nu}))) \\ F_\nu(\tau_1 \ldots \tau_{n_\nu}, \tau'_1 \ldots \tau'_{m_\nu}). \end{aligned} \tag{30}$$

We focus on the third order two body contribution:

$$S_A^{(3)}(t) = \left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^t \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_1 \mathrm{Im}(\langle E_d^\dagger(t)V_a(t)H_{int,-}(t_3)H_{int,-}(t_2)H_{int,-}(t_1)\rangle). \tag{31}$$

(S_B can be obtained similarly). In fourth order it contains single particle parts $S_A^{(3)}(t)$, $\sim \mu_A^4$ and two body parts $S_A^{(3)}(t)$, $\sim \mu_a^2\mu_b^2$. As before, we only consider the lowest order two body $\sim \mu_A^2\mu_B^2$ terms, which can show collective effects.

$S_A^{(3)}(t)$ can be represented by the six close time path loop (CTPL) diagrams shown in Fig. 3 (For rules see [14]):

$$\begin{aligned} S_A^{(3)}(t) = S_{ia}^{(3)}(t) + S_{ib}^{(3)}(t) + S_{iia}^{(3)}(t) + S_{iib}^{(3)}(t) \\ +S_{iii}^{(3)}(t) + S_{iv}^{(3)}(t) - c.c.. \end{aligned} \tag{32}$$

Paths (ia) and (ib), include two photon transitions. They have a negative sign, due the odd number of interactions on the right side of the diagram:

$$\begin{aligned} S_{ia}^{(3)}(t) = -\left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^t \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_1 \int_{t_0}^t \mathrm{d}t_3 \langle V_A(t)V_A^\dagger(t_1)\rangle\langle V_B(t_3)V_B^\dagger(t_2)\rangle\langle E^\dagger(t_3)E_d^\dagger(t)E(t_2)E(t_1)\rangle, \\ S_{ib}^{(3)}(t) = -\left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^t \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_1 \int_{t_0}^t \mathrm{d}t_3 \langle V_A(t)V_A^\dagger(t_2)\rangle\langle V_B(t_3)V_B^\dagger(t_1)\rangle\langle E^\dagger(t_3)E_d^\dagger(t)E(t_2)E(t_1)\rangle. \end{aligned} \tag{33}$$

We can combine the two paths by interchanging the times t_1 and t_2 in $S_{ib}^{(3)}$ and introducing

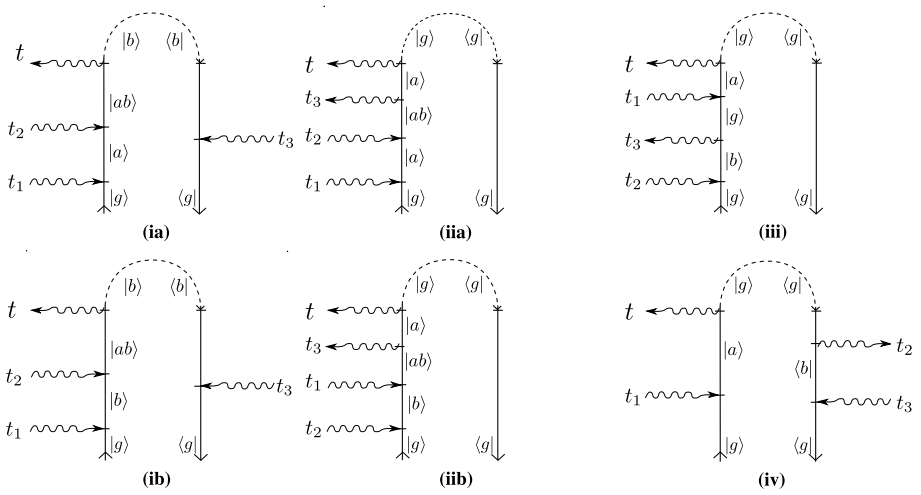

Figure 3: The six closed time path loop (CTPL) diagrams for the two body pump probe signal generated at atom A Eq. (32). For rules see Ref. 14. Here the observation time t is always *chronologically* the last but is obviously not the last along the loop. (i) Eq. (33) and (ii) Eq. (35) use TPA pathways (two absorption processes followed by two emissions along the loop), (iii) Eq. (37) and (iv) Eq. (38) are emission pathways (absorption, emission, absorption, emission) along the loop. Similar diagrams apply to the signal genrated at system B by interchanging the indices a and b.

a field commutator $[E(t_1), E(t_2)]$, which vanishes in this case:

$$\begin{aligned} S_i^{(3)}(t) &= S_{ia}^{(3)}(t) + S_{ib}^{(3)}(t), \\ S_i^{(3)}(t) &= -\left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_3 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E^\dagger(t_3) E_d^\dagger(t) E(t_2) E(t_1)\rangle. \end{aligned} \tag{34}$$

Repeating the same steps for pathways (iia) and (iib), we obtain:

$$\begin{aligned} S_{iia}^{(3)}(t) &= \left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_1 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) E^\dagger(t_3) E(t_2) E(t_1)\rangle, \\ S_{iib}^{(3)}(t) &= \left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_2 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) E^\dagger(t_3) E(t_2) E(t_1)\rangle, \\ S_{ii}^{(3)}(t) &= S_{iia}^{(3)}(t) + S_{iib}^{(3)}(t), \\ S_{ii}^{(3)}(t) &= \left(\frac{\imath}{\hbar}\right)^3 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_1 \int_{t_0}^{t_3} \mathrm{d}t_2 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) E^\dagger(t_3) E(t_2) E(t_1)\rangle. \end{aligned} \tag{35}$$

Alternatively Eq. (35) can be obtained directly from Eq. (34) by changing the temporal arguments of $V_B^\dagger$ and $V_A^\dagger$ and relabeling of the times.

Pathway (iii), which represents a ground state bleaching process is given by:

$$S^{(3)}_{(iii)}(t) \;=\; \Big(\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) E(t_1) E^\dagger(t_3) E(t_2)\rangle. \tag{36}$$

We shall bring the product of field operators into a normal form and add a commutator (see Eq. (A3)):

$$\begin{aligned} S^{(3)}_{(iii)}(t) \;=\; & \Big(\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) E^\dagger(t_3) E(t_2) E(t_1)\rangle \\ & + \Big(\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) [E(t_1), E^\dagger(t_3)] E(t_2)\rangle. \end{aligned} \tag{37}$$

Finally diagram (iv) which represents excited state emission gives:

$$S^{(3)}_{(iv)}(t) \;=\; \Big(\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_3 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E^\dagger(t_3) E(t_2) E_d^\dagger(t) E(t_1)\rangle. \tag{38}$$

as we did in Eq. (37), we shall use Eq, (A3) and recast it as:

$$\begin{aligned} S^{(3)}_{(iv)}(t) \;=\; & \Big(\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_3 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) E^\dagger(t_3) E(t_2) E(t_1)\rangle \\ & + \Big(\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_3 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E^\dagger(t_3) [E(t_2), E_d^\dagger(t)] E(t_1)\rangle. \end{aligned} \tag{39}$$

Upon combining pathways (i)-(iv), we find that the stimulated contributions proportional to $\langle E_d^\dagger(\tau_4) E^\dagger(\tau_3) E(\tau_2) E(\tau_1)\rangle$ interfere destructively and cancel out, leaving only the spontaneous emission terms:

$$\begin{aligned} S^{(3)}_{A}(t) \;=\; & \Big(-\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E_d^\dagger(t) [E(t_1), E^\dagger(t_3)] E(t_2)\rangle \\ & + \Big(-\frac{\imath}{\hbar}\Big)^3 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_3 \langle V_A(t) V_A^\dagger(t_1)\rangle \langle V_B(t_3) V_B^\dagger(t_2)\rangle \langle E^\dagger(t_3) [E(t_2), E^\dagger(t)_d] E(t_1)\rangle. \end{aligned} \tag{40}$$

Here the commutator $[E(t_1), E^\dagger(t_3)]$ appears, $E(t) = \sum_s C_s e^{-\imath\omega_s t} a_s$ which is directly connected to the commutator $[a_s, a_{s'}^\dagger] = \delta_{ss'}$. Eq. (40) describes a process, where a photon is first absorbed by system B. Then another photon is spontaneously emitted and absorbed

by system A. This term scales like linear response times the spontaneous emission rate, it describes radiative transfer.

Obviously two photon absorption resonances $\omega_\alpha + \omega_\beta = \omega_a + \omega_b$ of two uncoupled systems do not occur when the driving fields are classical. The mechanism of interference presented in [7] was different, from the destructive interference mechanism described here. These details will be discussed below.

We now discuss the observation of two body resonances. The most obvious observable is the photon number, so that in the experiment the change of the photon numbers is detected for the two body part $\Delta_{AB} n_{ph}$. In the following, we will use the conservation of the sum of photon number and exciton number implied by the RWA Hamilton operator. The change in photon numbers will depend on the following probabilities: The excitation probability of P_{ab} means that two photon are absorbed (counts twice) and the excitation probability of only system A P_a and of only system B P_b (we assume that both photons have equal frequency and are resonant to the two photon absorption):

$$\Delta_{AB} n_{ph} = -2P_{ab}(t) - P_a(t) - P_b(t). \tag{41}$$

Now, in the stimulated (emission and TPA) pathways absorption, we know that $P_{ab}(t)$ and $P_a(t)$ cancel and that $P_{ab}(t)$ and $P_b(t)$ cancel. So for the stimulated pathways, we get:

$$\Delta_{AB} n_{ph} = 0. \tag{42}$$

These arguments on a matter perspective [14, 16] are consistent with the more general results of this section, where we showed that the stimulated two body part vanishes. *One photon observables do not show collective resonances between uncoupled systems.* Since our Hamiltonian connects the photon number with the exciton number, the photon number itself is a single particle observable like the population of state a or state b and therefore vanishes.

IV. CONCLUSIONS

Since our analysis shows that two photon absorption vanishes by interference, it will be of interest to identify an observable, that does reveal the resonances of $P_{ab}(t)$. We now show that this can be done by two photon counting (Hanbury-Brown-Twiss measurements)[11]. For our entangled photon state Eq. (18), the change in the photon-photon correlation

$\Delta_{AB,ph-corr}$ is attributed to any buildup of probability, that the combined system is in either system A or system B or both, which will cause an reduction of the photon-photon correlation:

$$\Delta_{AB,ph-corr} = -P_{ab}(t) - P_a(t) - P_b(t). \tag{43}$$

Since $P_{ab}(t)$ now does not enter with a factor two (unlike Eq. (41) the stimulated contributions can only cancel with one of the two other contributions $P_a(t)$ or $P_b(t)$, and we have:

$$\Delta_{AB,ph-corr} = -P_b(t). \tag{44}$$

The interference mechanism, which caused the cancellation for the stimulated signal and the photon number, does not lead to a full cancellation, two photon absorption between the two systems might be observed. The term $P_b(t)$ remains. However, since the stimulated part $P_{ab}(t)$ and $P_b(t)$ are the same, we can reformulate this quantity as for the stimulated part:

$$\Delta_{AB,ph-corr} = P_{ab}(t). \tag{45}$$

Now the remaining term was used in [7] for the derivation of a two photon absorption. In order to verify the existence for the attenuation of the photon-photon correlation, we evaluate $P_{ab}(t)$ or $P_b(t)$, and discuss the possible interference due to the lack of time ordering of the two absorptions. Since uncoupled systems do not include the information on which path was selected by the system, because the interaction matrix elements of system A are not changed by a prior interaction of system B (and vice versa). The calculation of $P_{ab}(t)$ for the example of an entangled photon pair produced by a cascade state showed, that two body resonances are indeed present. (cf. Eq.(20))

The changes in the two photon correlation function should be visible in the attenuation of the photon-photon correlation function. The difference of the photon-photon correlation of an entangled photon source measured with and without the sample is proportional to $P_{ab}(t)$. Collective resonances are visible in the photon photon correlation function photon statistics and not in single particle quantities, such as a two photon absorption.

In summary, in this paper, we have analyzed the destructive interference mechanism of stimulated two body contributions from uncoupled systems. We found that for single particle observables (either matter or photon), no two body contributions can be measured

in uncoupled atoms by stimulated signals such as pump probe. That means also, that no two photon resonances can be observed in this case. However these resonances are measurable in the photon-photon correlation function.

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Appendix A: Fourth order calculation of excited state populations

Using the diagramatric rules given in [14], we obtain from Fig. 1,

$$\begin{aligned}
P_{ab}(t) \;=\; & \Big(-\frac{\imath}{\hbar}\Big)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_4 \langle g_A|V_A(t_2)V_A^\dagger(t_1)|g_A\rangle\langle g_B|V_B(t_4)V_B^\dagger(t_3)|g_B\rangle \\
& \langle E^\dagger(t_2)E^\dagger(t_4)E(t_3)E(t_1)\rangle \\
& + \Big(-\frac{\imath}{\hbar}\Big)^4 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_4 \langle g_A|V_A(t_2)V_A^\dagger(t_1)|g_A\rangle\langle g_B|V_B(t_4)V_B^\dagger(t_3)|g_B\rangle \\
& \langle E^\dagger(t_2)E^\dagger(t_4)E(t_3)E(t_1)\rangle \\
& + \Big(-\frac{\imath}{\hbar}\Big)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_2 \langle g_A|V_A(t_2)V_A^\dagger(t_1)|g_A\rangle\langle g_B|V_B(t_4)V_B^\dagger(t_3)|g_B\rangle \\
& \langle E^\dagger(t_2)E^\dagger(t_4)E(t_3)E(t_1)\rangle \\
& + \Big(-\frac{\imath}{\hbar}\Big)^4 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_2 \langle g_A|V_A(t_2)V_A^\dagger(t_1)|g_A\rangle\langle g_B|V_B(t_4)V_B^\dagger(t_3)|g_B\rangle \\
& \langle E^\dagger(t_2)E^\dagger(t_4)E(t_3)E(t_1)\rangle. \qquad \text{(A1)}
\end{aligned}$$

We used that, since $E(t) = \sum_s A_s e^{\imath \mathbf{k}_s \cdot \mathbf{r} - \imath \omega_s t} a_s$ and since $[a_s, a_{s'}] = 0$ the commutators $[E(t_1), E(t_2)]$ vanish. Similary from Fig. 2, we have:

$$
\begin{aligned}
P_a(t) \;=\; & -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_2 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_2) E(t_1) E^\dagger(t_4) E(t_3) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_2 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_2) E^\dagger(t_4) E(t_3) E(t_1) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_2) E^\dagger(t_4) E(t_3) E(t_1) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_4 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_4) E(t_3) E^\dagger(t_2) E(t_1) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_4 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_2) E^\dagger(t_4) E(t_3) E(t_1) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_2 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_2) E^\dagger(t_4) E(t_3) E(t_1) \rangle .
\end{aligned}
\tag{A2}
$$

We can substitute the relation

$$
\langle E^\dagger(t_2) E(t_1), E^\dagger(t_4) E(t_3) \rangle = \langle E^\dagger(t_2) [E(t_1), E^\dagger(t_4)] E(t_3) \rangle + \langle E^\dagger(t_2) E^\dagger(t_4) E(t_3) E(t_1) \rangle . \tag{A3}
$$

In the first and forth terms and collect the terms to obtain:

$$
\begin{aligned}
P_a(t) \;=\; & -\left(-\frac{\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t} \mathrm{d}t_4 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_4) E^\dagger(t_2) E(t_3) E(t_1) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t_1} \mathrm{d}t_4 \int_{t_0}^{t_4} \mathrm{d}t_3 \int_{t_0}^{t} \mathrm{d}t_2 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_2) [E(t_1), E^\dagger(t_4)] E(t_3) \rangle \\
& -\left(\frac{-\imath}{\hbar}\right)^4 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_3 \int_{t_0}^{t_3} \mathrm{d}t_4 \langle g_A | V_A(t_2) V_A^\dagger(t_1) | g_A \rangle \langle g_B | V_B(t_4) V_B^\dagger(t_3) | g_B \rangle \\
& \langle E^\dagger(t_4) [E(t_3), E^\dagger(t_2)] E(t_1) \rangle .
\end{aligned}
\tag{A4}
$$

The first term is the sum of all six stimulated terms. The other two are the spontaneous terms.

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[18] *Nonlinear* for the response means nonlinear with respect to the optical light field intensity operator $E^{\dagger}(\cdot)E(\cdot)$ at the sample. For classical fields this also implies nonlinear in the external field intensity. However this is not the case for entangled fields where the signal scales linearly in the intensity entering the entangled photon pairs generating device (often a crystal), even though it is also quadratic in $E^{\dagger}(\cdot)E(\cdot)$ at the sample.

[19] It is possible to use a symmetric form of O_{-} and O_{+} given by a unitary transformation from

O_L and O_R [17]. However we have chosen an asymmetric non unitary definition in which O_- and O_+ are normalized differently. With this choice the propagators in Liouville space have a more compact form.