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Quantized-field approach to parametric mixing and pressure-induced resonances: Schrödinger picture

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An interpretation of collision-induced extra resonances in multiwave mixing is constructed using a fully quantum-mechanical calculation carried out in the Schrödinger representation. The phase-matched signal is seen to arise as an interference between the amplitudes for scattering of the incident fields at different atomic sites. When collisions occur, the separation of the signal into a collision-induced resonance plus a background term appears naturally in this approach. The origin of the phase-matching condition, conservation of energy (and breaking of the Manley-Rowe relations), the role played by relaxation mechanisms, and the fact that the fields need not be temporally coherent to produce the extra resonances, all can be easily understood within the context of this calculation.

INTRODUCTION

Since their first observation by Prior *et al.*,[1] the pressure-induced extra resonances in four-wave mixing[2] (PIER 4) have been the subject of a considerable amount of literature. In spite of the fact that the theory[3] was well established and was in perfect agreement with the experimental results, there was no consensus as to the physical origin of the resonances. The first interpretation relied on the "destruction of destructive interference" that appears when four-wave-mixing emission is calculated perturbatively from the optical Bloch equations; however, it was shown that an alternative description of the extra resonances, as well as that for collisionally aided radiative excitation,[4] could be given based on energy conservation arguments.[5] Another interpretation was related to the connection between extra resonances and collisional redistribution of radiation that emerges from the microscopic calculation of the collisionally excited dressed-atom coherence that generates the four-wave-mixing emission.[6] However, the relation between the two-phenomena was not totally clear since collisional redistribution of radiation is a single-atom effect while four-wave-mixing emission is a collective effect.[7,8]

To clarify the physics of the extra resonances, we have shown that extra resonances can also be observed in the nonlinear spectroscopy of a single atom.[5] The new resonances that appear in this situation can be observed on the total fluorescence. These resonances can be understood either as resulting from the collisionally aided creation of a Raman coherence or from the interference between two quantum paths, each path involving a collisionally aided excitation.[9] It should be emphasized that the paths considered here involve usual state vectors and are not the double-sided diagrams used in the first interpretation of the extra resonances.

To understand the origin of the collective behavior in the four-wave-mixing emission, we developed two models appropriate for two-level atoms. In the first model, we used a semiclassical dressed-atom model to show that the collisionally aided excitation of the upper dressed state is temporally and spatially modulated.[10] This excitation thus induces a grating, which diffracts the incident waves and produces four-wave-mixing emission. The intensity of the emission is maximum when the amplitude of the collisionally aided grating is maximum, i.e., when the condition for the observation of extra resonances is satisfied. In a second paper,[11] we extended this model and used a fully quantum description of the electromagnetic fields. In the Heisenberg approach, we showed that the physical interpretation is essentially similar to the one developed in the preceding approach. We also indicated why the four-wave-mixing emission depends on the collisionally excited dressed-atom coherence in the Schrödinger approach.

It is the aim of this paper to give a final and unambiguous interpretation of these extra resonances in parametric mixing. Our model is developed for the case of a three-level atom, but the theory can be extended to a more complicated situation. We have chosen here to discuss the case of a three-level atom because many experimental situations can be described by such a model and also because the Schrödinger picture that we develop here provides very clear pictures for such an atom. We first recall in Sec. I the results obtained using the optical Bloch-equation approach with classical electromagnetic fields. We then calculate the energy exchanged between the atoms and the applied fields and show that the collisionally aided terms have a behavior different from the background terms. More precisely, we show that, in contrast to the background terms, the collisionally aided terms do not verify the Manley-Rowe relations,[12] this result not being consistent with some earlier pictures of the extra-resonances. In Sec. II, we address the problem of the interaction of a set of atoms with the quantized fields. We show that the parametric mixing results from the scattering of the radiation by a set of atoms and that the phase-matching condition appears as a requirement to obtain a constructive interference of the scattering amplitude by different atoms. When collisional dephasing is introduced, new scattering processes involving a collisionally aided excitation must be considered. The conditions for which the scattering amplitudes associated with different atoms constructively interfere are seen to lead to the phase-matching condition and the resonance condition for the extra resonances. Our analysis is supported by a calculation made in the Schrödinger picture where the dephasing collisions are considered *ab initio*. Even if this calculation is essential to support our interpretation, we want to emphasize that the heart of the paper is the diagrammatic physical interpretation given in the first part of Sec. II. Two complementary arguments are given in Appendix A and B. In Appendix A we calculate the parametric emission in the dressed-state basis and relate the parametric emission in the absence of collisional damping to Dicke superradiance.[13] These two processes lead to a spontaneous-emission rate proportional to the square of the number of atoms. In the case of collisions, we establish the connection between the extra resonances in parametric mixing, the collisionally excited Raman coherences considered earlier, and the interference phenomena described in Sec. II. In Appendix B we describe the relaxation mechanism by an interaction with a bath. This approach permits us to follow the evolution of the quantum numbers of the bath. To have an interference, the final quantum numbers of the bath should be the same, independent of the path followed by the system; a behavior that is found when we consider the various paths leading to the emission of a parametric photon. This approach thus strengthens our interpretation in terms of interference of scattering amplitudes.

I. CASE OF CLASSICAL FIELDS

A. Three-wave-mixing emission

We consider a set of three-level atoms [ground state a, excited states b and b' (see Fig. 1)] interacting with two classical electromagnetic fields:

$$\mathbf{E}(\mathbf{r},t)=E\mathbf{e}\cos(\omega t-\mathbf{k}\cdot\mathbf{r}+\theta) \,, \quad (1a)$$

$$\mathbf{E}'(\mathbf{r},t)=E'\mathbf{e}'\cos(\omega' t-\mathbf{k}'\cdot\mathbf{r}+\theta') \,. \quad (1b)$$

The first field is nearly resonant with the a-b transition and we denote by $\Delta=\omega-\omega_0$ its frequency detuning from resonance. The second field is nearly resonant with the a-b' transition and we define its detuning by $\Delta'=\omega'-\omega_0'$. The resonance Rabi frequencies associated with these two fields are denoted by Ω_1 and Ω_1',

$$\Omega_1=-\frac{d_{ab}E}{\hbar} \,, \quad (2a)$$

$$\Omega_1'=-\frac{d_{ab'}E'}{\hbar} \,, \quad (2b)$$

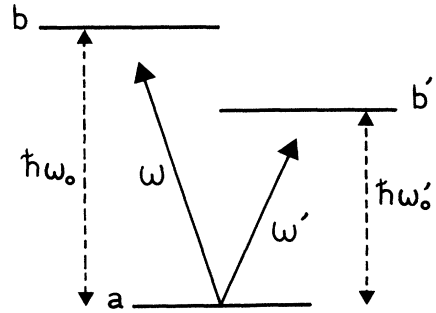

FIG. 1. Scheme of the energy levels of the atoms considered in this paper. All the transitions (a-b, b-b', b'-a) are assumed to be dipole allowed.

where d_{ab} and $d_{ab'}$ are dipole-moment matrix elements, assumed real. It is also assumed that an electric dipole transition between levels b and b' is allowed and we denote by $d_{bb'}$ the corresponding dipole-moment matrix element.[14] (For simplicity, it is assumed that the incident and emitted fields are all polarized along the same direction and that this polarization is consistent with the various selection rules.)

The radiative lifetimes of the excited states b and b' are Γ_b and $\Gamma_{b'}$, respectively. Apart from radiative decay, the atoms undergo collisional relaxation. We assume that the active atoms are perturbed by a buffer gas and that the collisions are dephasing in nature, inducing a decay of the atomic state coherences but not of the atomic state populations. The relaxation rate of the atomic state coherence $i-j$ due to collisions is denoted by γ_{ij}. We assume that the conditions of the impact approximation are satisfied and, in particularly, that $|\Delta|$ and $|\Delta'|$ are small compared to τ_c^{-1} where τ_c is the typical duration of a collision. On the other hand, we assume that $|\Delta|$ and $|\Delta'|$ are large compared to the widths of the a-b and a-b' transitions but that $|\Delta-\Delta'|$ remains small compared to $|\Delta|$ and $|\Delta'|$. We also assume that $|\Omega_1/\Delta|$ and $|\Omega_1'/\Delta'|$ are very small compared to unity. To second order in the incident fields, the coherence $\rho_{bb'}$ of the atomic density matrix (which is the source term for the radiation at frequency $\omega-\omega'$) is equal to

$$\rho_{bb'}=\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\left[1+\frac{\gamma_{bb'}^a}{\Gamma_{bb'}-i\delta}\right] \times e^{-i[(\omega-\omega')t-(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}+\theta-\theta']} \,, \quad (3)$$

where $\gamma_{bb'}^a$ is the collisional factor introduced by Bloembergen, Loten, and Lynch,[3]

$$\gamma_{bb'}^a=\gamma_{ba}+\gamma_{b'a}^*-\gamma_{bb'} \,, \quad (4a)$$

and

$$\Gamma_{bb'}=\frac{\Gamma_b}{2}+\frac{\Gamma_{b'}}{2}+\gamma_{bb'} \,, \quad (4b)$$

$$\delta=\Delta-\Delta' \,. \quad (4c)$$

One can remark that $\gamma^a_{bb'}$ is generally complex because γ_{ij} is the sum of a real component associated with the pressure broadening and an imaginary component associated with the pressure shift. The component of the electric dipole moment associated with the field radiated at frequency $\omega''=\omega-\omega'$ is

$$d(\omega'')=d_{bb'}(\rho_{bb'}+\rho^*_{bb'}) \ . \qquad (5)$$

The preceding calculation has been developed for a single atom. Now we look for the effects that originate from the cooperative emission of N atoms enclosed in a volume V. We assume that this volume is a parallelepiped with the longitudinal dimension L much larger than the transverse dimension d and also assume that $d \gg \lambda_0$ (λ_0 is the wavelength of any of the three fields considered here) and that $d^2/L\lambda_0 \gg 1$.

The electric fields radiated by the N dipoles interfere constructively in the forward direction if the phase-matching condition

$$\mathbf{k}''=\mathbf{k}-\mathbf{k}' \qquad (6)$$

is fulfilled. We assume here that this condition is satisfied. The mean intensity I'' of the three-wave-mixing emission is obtained by solving the Maxwell equations in the slowly varying envelope approximation.[15] The resulting intensity is

$$I''=\left[\frac{N}{S}\right]^2 \frac{\omega''^2}{2\varepsilon_0^2 c^2} d^2_{bb'}|\rho_{bb'}|^2 \ , \qquad (7)$$

where $S=d^2$.

Even though this theory involves only classified fields, it is possible to express the result in terms of a rate of emission of photons having frequency ω''. To obtain this rate Γ, we multiply the mean value of the Poynting vector $\varepsilon_0 c I''$ by the surface S of the parallelepiped and divide this result by the energy quantum $\hbar\omega''$ to obtain

$$\Gamma=\frac{\varepsilon_0 c I'' S}{\hbar\omega''} \ . \qquad (8)$$

Finally, using (3), (7), and (8), we find[16]

$$\Gamma=\frac{N^2}{S}\frac{\omega''}{2\varepsilon_0 c\hbar} d^2_{bb'}\left[\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right]^2 \left|1+\frac{\gamma^a_{bb'}}{\Gamma_{bb'}-i\delta}\right|^2 \ . \qquad (9)$$

In the presence of collisions the three-wave-mixing emission exhibits a resonance around $\delta=0$.[17] This resonance had been first predicted by Bloembergen, Loten, and Lynch[3] and observed by Prior *et al.*[1] The parametric emission given by formula (9) appears as a coherent emission proportional to N^2 in the phase-matched direction. This square law dependence was considered to be a problem when it was shown that the PIER 4 extra resonance could be connected to collisionally aided redistribution of radiation,[6] which is usually a process whose intensity is proportional to N. We shall return to this point in Sec. II.

B. The Manley-Rowe relations

It is well known that in the case of nonresonant harmonic generation, there exists a relation between the energies exchanged among the different electromagnetic fields.[12] The Manley-Rowe relations[12,15] state that the total field energy remains constant in the steady-state regime, the energy taken from one field being converted to another. In a quantized-field picture, this implies that for each ω photon absorbed in Fig. 2, there is one ω'' photon and one ω' photon emitted. It is shown below that this relation does not hold for the pressure-induced contribution to the three-wave-mixing generation. Actually, it is well known that the Manley-Rowe relations are valid only in the absence of damping, so that one should not expect that they remain true in the case of PIER resonances. However, since some of the earlier pictures of the PIER make use of this conservation of the photon number, we want to show explicitly that the Manley-Rowe relations are not true for the PIER resonances and that the number of photons emitted in a coherent fashion at frequencies ω' and ω'' are not equal at the center of the PIER resonance.

We consider atoms interacting with three incident classical fields of frequencies ω, ω', and ω''. To second order in the input fields, the atomic coherences that are involved in the three-wave-mixing process are $\rho_{bb'}$ given in formula (3), and ρ_{ba} and $\rho_{b'a}$ given by

$$\rho_{ba}=\frac{\Omega_1'\Omega_1''}{4\Delta\Delta'}e^{-i[(\omega'+\omega'')t-(\mathbf{k}'+\mathbf{k}'')\cdot\mathbf{r}+\theta'+\theta'']} \ , \qquad (10a)$$

$$\rho_{b'a}=\frac{\Omega_1\Omega_1''}{4\Delta\Delta'}e^{-i[(\omega-\omega'')t-(\mathbf{k}-\mathbf{k}'')\cdot\mathbf{r}+\theta-\theta'']} \ , \qquad (10b)$$

where $\Omega_1''=-d_{bb'}E''/\hbar$, and θ'' is the phase of the classical field E''. The mean energy exchanged between an atom and the field of frequency ω is equal to

$$W(\omega)=\left\langle E(t)\frac{d}{dt}[d(\omega)]\right\rangle_{\rm av} \ . \qquad (11)$$

Assuming that the phase-matching condition (6) is fulfilled and using (10a) we find

$$\frac{W(\omega)}{\hbar\omega}=\frac{\Omega_1\Omega_1'\Omega_1''}{4\Delta\Delta'}\sin(\theta'+\theta''-\theta) \ . \qquad (12a)$$

Similarly, using (10b), we find

$$\frac{W(\omega')}{\hbar\omega'}=\frac{\Omega_1\Omega_1'\Omega_1''}{4\Delta\Delta'}\sin(\theta-\theta'-\theta'') \ . \qquad (12b)$$

Finally, if we suppose that the resonance condition ($\delta=0$) is satisfied and that $\gamma^a_{bb'}$ is real, it follows from (11), (5), (3), and (6) that

$$\frac{W(\omega'')}{\hbar\omega''}=\frac{\Omega_1\Omega_1'\Omega_1''}{4\Delta\Delta'}\left[1+\frac{\gamma^a_{bb'}}{\Gamma_{bb'}}\right]\sin(\theta-\theta'-\theta'') \ . \qquad (13)$$

In the absence of collisions ($\gamma^a_{bb'}=0$), Eqs. (12) and (13) imply the Manley-Rowe relations

$$\frac{W(\omega)}{\hbar\omega}=-\frac{W(\omega')}{\hbar\omega'}=-\frac{W(\omega'')}{\hbar\omega''} \ . \qquad (14)$$

For each photon of frequency ω that is absorbed, there is one photon of frequency ω' and one of frequency ω'' emitted. This property suggests the well-known scheme (Fig. 2) associated with a parametric process.

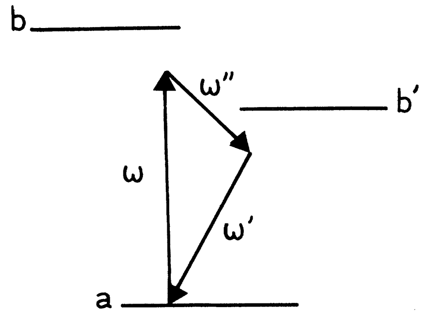

FIG. 2. Usual scheme of the parametric mixing process. For each ω photon absorbed, there is one ω'' photon and one ω' photon emitted.

It is clear from Eqs. (12) and (13) that the Manley-Rowe relations are no longer valid in the presence of collisional damping ($\gamma^{a}_{bb'}\neq 0$). The collision-induced change in the coherent emission at frequency ω'' is not connected with a similar change at the other frequencies. It has been sometimes argued that the scheme of Fig. 2 remains valid for emission associated with the extra resonance, the only difference being that the energy levels are shifted during the collision process. The difference between (12) and (13) shows clearly that this is not the case and that a scheme similar to the one of Fig. 2 cannot be applied to the pressure-induced extra resonance. To understand physically the origin of the extra resonances, one has to consider other pictures. One purpose of Sec. II is to give a better physical understanding of these extra resonances.

We have shown that the intensity of the parametric emission at ω'' does not coincide in the presence of collisions with that at ω'. Such a result may look surprising in terms of energy conservation. In fact, the difference between these two rates of emission is compensated by a change in the spontaneous emission from level b'. This rate of spontaneous emission is equal to $\Gamma_{b'}\rho_{b'b'}$. If we calculate the component of $\rho_{b'b'}$ proportional to $\Omega_1\Omega_1'\Omega_1''$ we find by solving the density matrix equations to third order and keeping the term of interest that

$$\Gamma_{b'}\rho^{(I)}_{b'b'}=\frac{\Omega_1\Omega_1'\Omega_1''}{4\Delta\Delta'}\frac{\gamma^{a}_{bb'}}{\Gamma_{bb'}}\sin(\theta-\theta'-\theta'') \ . \tag{15}$$

This term is essentially identical to the one considered previously[9] for the observation of PIER in nonlinear spectroscopy. It can be positive or negative depending on the sign of $(\theta-\theta'-\theta'')$, but the total fluorescence from level b' is of course positive. By comparing (12), (13), and (15), one sees that the difference between the rates of emission at ω'' and ω' can be attributed to the spontaneous emission from level b'.

II. CASE OF QUANTIZED FIELDS

A. Physical interpretation

In this subsection, a qualitative description of signal formation is given that emphasizes its physical origin. This interpretation is supported by the algebra presented in Sec. II B and in the appendixes.

1. Absence of collisional damping

We first discuss the situation where the atoms are not subjected to collisional damping. We assume that initially all the atoms are in the ground state a and that the initial state of the field is $|n,n',0\rangle$, where n and n' are the number of photons in the modes ω and ω'. We seek the probability of having one photon emitted in the mode ω''. The most obvious amplitude leading to emission of an ω'' photon is shown in Fig. 2, where an atom absorbs one photon from mode ω and emits one photon each into modes ω'' and ω'. The scattering amplitudes associated with different atoms can interfere if it is not possible to detect which atom has really scattered the radiation. At the end of the process, the state of the atom that has scattered the radiation is the ground state a and thus coincides with the atomic state of the other atoms. During the scattering process, the atom receives a momentum equal to $\hbar(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')$. If the phase-matching condition is fulfilled, there is no transfer of momentum and, consequently, no possibility to distinguish which atom has scattered the radiation. In conclusion, the scattering amplitudes shown in Fig. 2 associated with different atoms interfere constructively when the photon ω'' is emitted in the phase-matching direction (Fig. 3). We have then to sum the scattering amplitudes and not the scattering probabilities. This is the origin of the enhancement of the emission in the direction $\mathbf{k}''=\mathbf{k}-\mathbf{k}'$ in the quantized-field approach.[18]

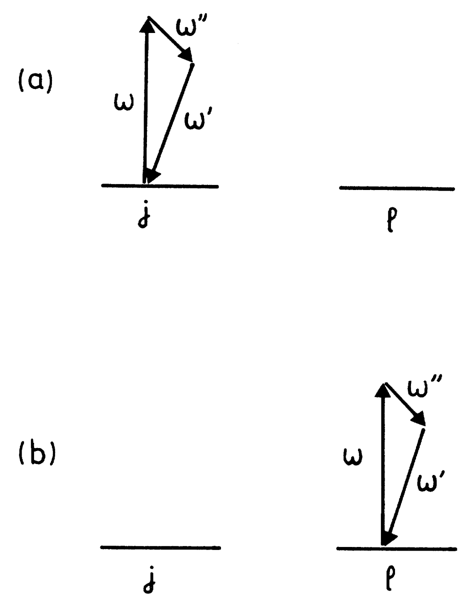

FIG. 3. Interference between the scattering amplitudes associated with atom j (a) and atom l (b). These two amplitudes constructively interfere when the phase-matching condition is fulfilled. The diagrams represented here correspond to the parametric emission in the absence of collisional damping.

2. *Case of collisional damping*

When the atoms undergo collisions, other interference phenomena involving two atoms can occur. Let us consider two atoms j and l. One amplitude [Fig. 4(a)] involves a parametric interaction (similar to the one described in the preceding section) for atom j (absorption of ω, emission of ω'' and ω') and a collisionally aided absorption of a photon ω' followed by a spontaneous emission of a photon of frequency ω_1' for atom l. Another amplitude [Fig. 4(b)] involves a collisionally aided absorption of a photon ω followed by the emission of photons ω'' and ω_1' by atom l, atom j remaining in its ground state. These two amplitudes can interfere if the final state for the two atoms and for the fields are the same. One can see that in both processes a photon ω is absorbed and two photons (ω'' and ω_1') are emitted [in the process shown in Fig. 4(a) there is an absorption of a photon ω' and an emission of a photon ω' with the net result that the number of ω' photons is unchanged]. The transfer of energy between atom l and its collision partner is $\hbar(\omega'-\omega_1')$ for the process shown in Fig. 4(a) and $\hbar(\omega-\omega''-\omega_1')$ for the process shown in Fig. 4(b). The condition of interference is thus $\omega=\omega'+\omega''$. Furthermore, the process shown in Fig. 4(b) is maximum when ω'' coincides with the atomic frequency $\omega_{bb'}$, which implies $\delta=0$. This is the resonance condition for PIER 4. Finally, we note that the transfer of momentum from the field is $\hbar(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')$ for atom j and $\hbar(\mathbf{k}'-\mathbf{k}'_1)$ for the atom l in Fig. 4(a). In Fig. 4(b) the transfers are 0 for atom j and $\hbar(\mathbf{k}-\mathbf{k}''-\mathbf{k}'_1)$ for atom l. The transfers are equal in the two processes, provided that the phase-matching condition is fulfilled. Since the number of pairs of atoms that can constructively interfere to provide phase-matched emission is proportional to $N(N-1)\sim N^2$, we have here an interference process that can explain the features of PIER 4.

Another interference occurs with the diagrams shown in Fig. 5. In the two cases [Figs. 5(a) and 5(b)], atoms j and l undergo collisions. In the diagram of Fig. 5(a), the photon ω'' is emitted by atom l while the photon ω'' is emitted by atom j in Fig. 5(b). For the two cases, there is absorption of one ω photon and one ω' photon and emission of one photon in the modes $\omega'',\omega_1',\omega_2'$. The energy exchanged between atom j and its collision partner X is $\hbar(\omega'-\omega_1')$ in Fig. 5(a) and $\hbar(\omega-\omega''-\omega_1')$ in Fig. 5(b). Similarly, the energy exchanged between atom l and its collision partner Y is $\hbar(\omega-\omega''-\omega_2')$ in Fig. 5(a) and $\hbar(\omega'-\omega_2')$ in Fig. 5(b). To have an interference, the transfers of Fig. 5(a) should be equal to the transfer of

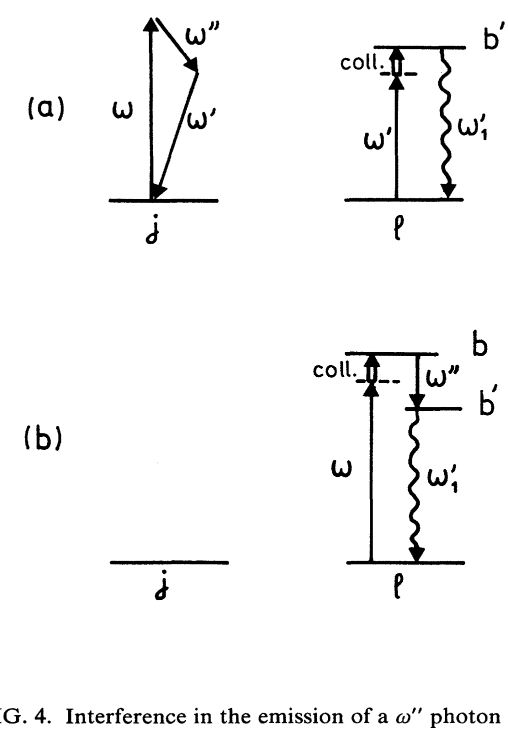

FIG. 4. Interference in the emission of a ω'' photon by a pair of atoms. In the process shown in (a), the ω'' photon is emitted by atom j through a parametric mixing process, while atom l emits a spontaneous photon of frequency ω_1' after absorbing a ω' photon. In the process shown in (b), the photons ω'' and ω_1' are emitted by atom l in a cascade that follows the collisionally aided excitation of level b. The diagrams shown in (a) and (b) can interfere when the phase-matching condition is fulfilled. If this is the case, it is not possible to state which atom has emitted the photon ω''. The diagrams shown here correspond to the term linear in buffer gas pressure in the rate of emission of a photon ω''.

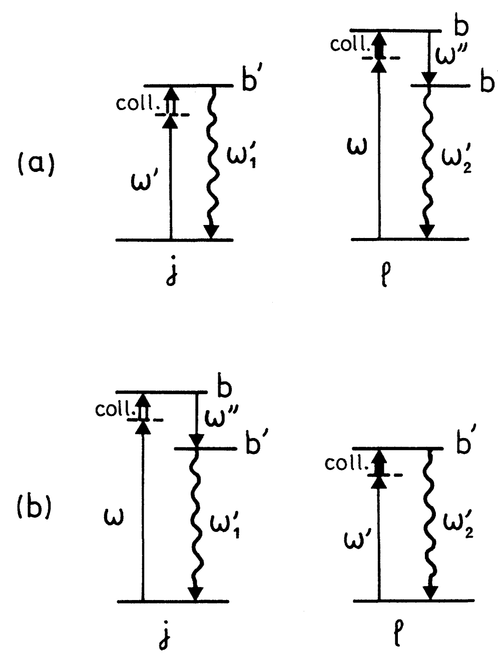

FIG. 5. Interference in the emission of a ω'' photon by a pair of atoms. In the process shown in (a), the ω'' photon is emitted by atom l while it is emitted by atom j in the process shown in (b). In the two processes, the atoms are collisionally excited. Atom j is excited to level b' in (a) and to level b in (b). Atom l is excited to level b in (a) and to level b' in (b). The diagrams shown in (a) and (b) can interfere when the phase-matching condition is fulfilled. It is then not possible to state which atom has emitted the ω'' photon. These diagrams correspond to the term quadratic in buffer gas pressure in the rate of emission of a photon ω''.

Fig. 5(b), which implies $\omega=\omega'+\omega''$. Furthermore, a resonance occurs when $\omega''=\omega_{bb'}$, i.e., when $\delta=0$. Finally, the transfers of momentum from the field to atom j are $\hbar(\mathbf{k}'-\mathbf{k}_1')$ and $\hbar(\mathbf{k}-\mathbf{k}''-\mathbf{k}_1')$ for the processes shown in Figs. 5(a) and 5(b), respectively. The transfers are equal when $\mathbf{k}=\mathbf{k}'+\mathbf{k}''$, i.e., when the phase-matching condition is fulfilled.

If we develop the factor $|1+\gamma_{bb'}^a/(\Gamma_{bb'}-i\delta)|^2$ found in formula (9), we find a term independent of the pressure, a term linear in $\gamma_{bb'}^a$, and a term varying as $(\gamma_{bb'}^a)^2$. The following calculation shows that the first term is described by the diagrams of Fig. 3, the term linear in $\gamma_{bb'}^a$, by the diagrams of Fig. 4, and the term quadratic in $\gamma_{bb'}^a$ by the diagrams of Fig. 5. One can understand this relationship without entering into the details of the calculations because the diagrams of Fig. 3 do not involve any collisions and are thus independent of the pressure; the diagrams of Fig. 4 involve only one collision and are thus connected with the term linear in pressure; and the diagrams of Fig. 5, which involve two collisions, are associated with the term quadratic in pressure. At this stage, this relation is only intuitive and the complete calculation presented now is necessary to establish this link on a rigorous basis.

B. Description in the bare atoms basis

1. Notation

The Hamiltonian H of the whole system can be split into two parts. The dominant term is H_0:

$$H_0=\sum_{j=1}^{N} h_0(j)+\sum_i \hbar\omega_i a_i^\dagger a_i+\hbar g\sum_j (S_j^+ a\, e^{i\Phi_j}+S_j^- a^\dagger e^{-i\Phi_j})+\hbar g'\sum_j (S_j'^+ a' e^{i\Phi_j'}+S_j'^- a'^\dagger e^{-i\Phi_j'}) . \quad (16)$$

The first term corresponds to the sum of the free Hamiltonian of the N atoms

$$h_0(j)=E_{b'}|b_j'\rangle\langle b_j'|+E_b|b_j\rangle\langle b_j|+E_a|a_j\rangle\langle a_j| . \quad (17)$$

The second term is the Hamiltonian of the free field. In particular, this term contains the contributions $\hbar\omega a^\dagger a$ and $\hbar\omega' a'^\dagger a'$ of the modes that are initially filled with photons (a and a' are the annihilation operators for the modes $\omega,\mathbf{k}$ and $\omega',\mathbf{k}'$, respectively). The next term describes the interaction between the atoms and the mode $(\omega,\mathbf{k})$ of the field. The operators S_j^+ and S_j^- are equal to $|b_j\rangle\langle a_j|$ and $|a_j\rangle\langle b_j|$, g is a coupling constant equal to $\Omega_1/2\sqrt{n}$ [where n is the number of photons in mode $(\omega,\mathbf{k})$], and Φ_j is a phase factor[19] equal to

$$\Phi_j=\mathbf{k}\cdot\mathbf{r}_j-\theta .$$

Similarly, the last term describes the interaction with the mode $(\omega',\mathbf{k})$ of the field. We have $S_j'^+=|b_j'\rangle\langle a_j|$, $S_j'^-=|a_j\rangle\langle b_j'|$, $g'=\Omega_1'/2\sqrt{n'}$ (n' is the number of photons in the mode $\omega',\mathbf{k}'$), and

$$\Phi_j'=\mathbf{k}'\cdot\mathbf{r}_j-\theta' .$$

The remaining part of the Hamiltonian $H_I=H-H_0$ described the interaction between the atoms and the modes of the field that are initially unpopulated. In particular, this term contains the coupling V'' with the mode $(\omega'',\mathbf{k}'')$, which is classically excited by the three-wave-mixing process,

$$V''=i\hbar g''\sum_j (S_j''^+ a'' e^{i\mathbf{k}''\cdot\mathbf{r}_j}-S_j''^- a''^\dagger e^{-i\mathbf{k}''\cdot\mathbf{r}_j}) , \quad (18)$$

with $S_j''^+=|b_j\rangle\langle b_j'|$, $S_j''^-=|b_j'\rangle\langle b_j|$, and $\hbar g''=-d_{bb'}\sqrt{\hbar\omega''/2\varepsilon_0 V}$, where V is the quantization volume. H_I also contains a term

$$V'=i\hbar g_1'\sum_j\sum_\mu (S_j'^+ a_\mu' e^{i\mathbf{k}_\mu'\cdot\mathbf{r}_j}-S_j'^- a_\mu'^\dagger e^{-i\mathbf{k}_\mu'\cdot\mathbf{r}_j}) , \quad (19)$$

which describes the interaction with the modes of the field having frequency close to ω_0' and which are initially not populated (we note $\hbar g_1'=-d_{b'a}\sqrt{\hbar\omega'/2\varepsilon_0 V}$).

2. Equation in the absence of collisional damping

Let us assume that the initial state of the system is $|a_1,\ldots,a_j,\ldots a_N\rangle\otimes|n,n',0\rangle$, which means that all the atoms are in the gound state and two modes of the field are occupied. The amplitude to have atom j in state b in the presence of $(n-1)$ photons $(\omega,\mathbf{k})$ and n' photons $(\omega',\mathbf{k}')$ is denoted by $C(b_j,n-1,n')$. Similarly, $C(b_j',n-1,n',\mathbf{k}'')$ describes atom j in state b' with $(n-1)$ photons $(\omega,\mathbf{k})$, n' photons $(\omega',\mathbf{k}')$, and one photon $(\omega'',\mathbf{k}'')$. Finally, $C(n-1,n'+1,\mathbf{k}'')$ describes a situation where all the atoms are in the ground state in the presence of $(n-1)$ photons $(\omega,\mathbf{k})$, $(n'+1)$ photons $(\omega',\mathbf{k}')$, and one photon $(\omega'',\mathbf{k}'')$.

The equations for the C coefficients, deduced from the Schrödinger equation,[20] are

$$\dot C(b_j,n-1,n')=-\frac{\Gamma_b}{2}C(b_j,n-1,n')-\frac{i\Omega_1}{2}e^{i\Phi_j}e^{-i\Delta t}C(n,n') , \quad (20a)$$

$$\dot C(b_j',n,n'-1)=-\frac{\Gamma_{b'}}{2}C(b_j',n,n'-1)-i\frac{\Omega_1'}{2}e^{i\Phi_j'}e^{-i\Delta' t}C(n,n') , \quad (20b)$$

$$\dot C(b_j',n-1,n',\mathbf{k}'')=-\frac{\Gamma_{b'}}{2}C(b_j',n-1,n',\mathbf{k}'')-g''e^{-i\mathbf{k}''\cdot\mathbf{r}_j}e^{i\Delta'' t}C(b_j,n-1,n')-i\frac{\Omega_1'}{2}e^{i\Phi_j'}e^{-i\Delta' t}C(n-1,n'+1,\mathbf{k}'') , \quad (20c)$$

$$\dot{C}(n-1,n'+1,\mathbf{k}'') = -i\frac{\Omega_1'}{2}\sum_j e^{-i\Phi_j'}e^{i\Delta' t}C(b_j',n-1,n',\mathbf{k}'') , \quad (20d)$$

$$\dot{C}(n,n'-1,\mathbf{k}_1') = -g_1'\sum_j e^{-i\mathbf{k}_1'\cdot\mathbf{r}_j}e^{i\Delta_1' t}C(b_j',n,n'-1) , \quad (20e)$$

$$\dot{C}(n-1,n',\mathbf{k}'',\mathbf{k}_1') = -g_1'\sum_j e^{-i\mathbf{k}_1'\cdot\mathbf{r}_j}e^{i\Delta_1' t}C(b_j',n-1,n',\mathbf{k}'') - i\frac{\Omega_1'}{2}\sum_j e^{-i\Phi_j'}e^{i\Delta' t}C(b_j',n-1,n'-1,\mathbf{k}'',\mathbf{k}_1') , \quad (20f)$$

$$\dot{C}(n-1,n'-1,\mathbf{k}'',\mathbf{k}_1',\mathbf{k}_2') = -g_1'\sum_j e^{-i\mathbf{k}_1'\cdot\mathbf{r}_j}e^{i\Delta_1' t}C(b_j',n-1,n',\mathbf{k}'',\mathbf{k}_2') - g_1'\sum_j e^{-i\mathbf{k}_2'\cdot\mathbf{r}_j}e^{i\Delta_2' t}C(b_j',n-1,n',\mathbf{k}'',\mathbf{k}_1') + \cdots , \quad (20g)$$

etc., where $\Delta''=\omega''-\omega_{bb'}$ and $\Delta_i'=\omega_i'-\omega_{b'a}$ (with $\omega_i'=ck_i'$).

We want to calculate the probability (linear in time and to order $\Omega_1^2\Omega_1'^2$) that a photon $\mathbf{k}''$ will be emitted, all the atoms being in their ground states. This probability is

$$P=P_{\rm I}+P_{\rm II}+P_{\rm III} , \quad (21)$$

with

$$P_{\rm I}=|C(n-1,n'+1,\mathbf{k}'')|^2 , \quad (22a)$$

$$P_{\rm II}=\sum_{\mathbf{k}_1'}|C(n-1,n',\mathbf{k}'',\mathbf{k}_1')|^2 , \quad (22b)$$

$$P_{\rm III}=\sum_{\mathbf{k}_1',\mathbf{k}_2'}|C(n-1,n'-1,\mathbf{k}'',\mathbf{k}_1',\mathbf{k}_2')|^2 . \quad (22c)$$

$P_{\rm I}$, $P_{\rm II}$, and $P_{\rm III}$ are, respectively, associated with processes where 0, 1, and 2 photons are spontaneously emitted in unoccupied modes on the $b'\rightarrow a$ transition. The comparison with the diagrams described previously shows that $P_{\rm I}$, $P_{\rm II}$, and $P_{\rm III}$ correspond to the contributions of the diagrams of Figs. 3, 4, and 5, respectively, to the signal. Let us first calculate $P_{\rm I}$. Using Eqs. (20a), (20c), and (20d) and the definitions of Φ_j and Φ_j', we find

$$C(n+1,n'+1,\mathbf{k}'')=2\pi e^{i(\Delta'+\Delta''-\Delta)(t/2)}\delta^{(t)}(\Delta'+\Delta''-\Delta)\sum_j\frac{\Omega_1\Omega_1' g'' e^{i(\Delta\mathbf{k})\cdot\mathbf{r}_j}}{4\left[\dfrac{\Gamma_b}{2}-i\Delta\right]\left[\dfrac{\Gamma_{b'}}{2}+i(\Delta''-\Delta)\right]} , \quad (23)$$

where

$$\delta^{(t)}(\Delta'+\Delta''-\Delta)=\frac{1}{2\pi}\int_{-t/2}^{t/2}d\tau\, e^{i(\Delta'+\Delta''-\Delta)\tau} \quad (24)$$

and

$$(\Delta\mathbf{k})\cdot\mathbf{r}_j=(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')\cdot\mathbf{r}_j+\theta'-\theta . \quad (25)$$

The amplitude $C(n-1,n'+1,\mathbf{k}'')$ is expressed as a sum over all atoms

$$C(n-1,n'+1,\mathbf{k}'')=\sum_j A_j e^{i(\Delta\mathbf{k})\cdot\mathbf{r}_j} . \quad (26)$$

In the limit considered in this paper ($|\Delta|$, $|\Delta'|\gg\Gamma_b,\Gamma_{b'}$), A_j is equal to

$$A_j\simeq-2\pi\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}g''\delta^{(t)}(\Delta'+\Delta''-\Delta)e^{i(\Delta'+\Delta''-\Delta)(t/2)} . \quad (27)$$

Using the relation

$$|\delta^{(t)}(\Delta'+\Delta''-\Delta)|^2\simeq\frac{t}{2\pi}\delta(\Delta'+\Delta''-\Delta) = \frac{t}{2\pi}\delta(\omega''+\omega'-\omega) , \quad (28)$$

we find

$$\frac{P_{\rm I}}{t}=2\pi\left[\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right]^2 g''^2\left[\sum_{j,l}e^{i\Delta\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_l)}\right]\times\delta(\omega''+\omega'-\omega) . \quad (29)$$

with $\Delta\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_l)=(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')\cdot(\mathbf{r}_j-\mathbf{r}_l)$. The rate of emission in the solid angle $d\Omega''$ is

$$d\Gamma_I=\frac{2\pi}{\hbar}\left[\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right]^2\frac{|d_{bb'}|^2\hbar\omega''}{2\varepsilon_0 V}\left|\sum_j e^{i(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')\cdot\mathbf{r}_j}\right|^2\rho(\hbar\omega'')d\Omega'' , \quad (30)$$

with the density of states

$$\rho(\hbar\omega'')=\frac{V}{8\pi^3}\frac{(\hbar\omega'')^2}{\hbar^3c^3} . \quad (31)$$

The angular integral that appears in the summation over $d\Omega''$ is well known.[21] If the Fresnel number $S/L\lambda$ is large compared to 1, we have

$$\int d\Omega''\left|\sum_j e^{i(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')\cdot\mathbf{r}_j}\right|^2=N^2\frac{\lambda''^2}{S} . \quad (32)$$

The rate of emission of photons ω'' is thus

$$\Gamma_I=\frac{N^2}{S}\frac{\omega''}{2\varepsilon_0 c\hbar}\left|\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right|^2|d_{bb'}|^2 . \quad (33)$$

This result coincides with the value obtained in the semiclassical approach when damping is neglected [see formula (9) with $\gamma^{a}_{bb'}=0$].

We show now that the contribution from $P_{\text{II}}+P_{\text{III}}$ vanishes when there are no collisions. This will establish the exact correspondence between the quantum result and the semiclassical result when there is no collisional damping. We first calculate $C(n-1,n',\mathbf{k}'',\mathbf{k}_1')$ and give its value in a form that will be suitable for the generalization to the case of collisional damping:

$$C(n-1,n',\mathbf{k}'',\mathbf{k}_1')=-\frac{i\Omega_1 g''g_1'}{2}\sum_j e^{i\Phi_j}e^{-i(\mathbf{k}_1'+\mathbf{k}'')\cdot\mathbf{r}_j}$$
$$\times\left[\int_0^t dt_1 e^{i\Delta_1' t_1}\int_0^{t_1}dt_2 e^{-(\Gamma_{b'}/2)(t_1-t_2)}e^{i\Delta'' t_2}\int_0^{t_2}dt_3 e^{-(\Gamma_b/2)(t_2-t_3)}e^{-i\Delta t_3}\right]$$
$$+\left[i\frac{g_1'\Omega_1'}{2}\sum_l e^{i\Phi_l'}e^{-i\mathbf{k}_1'\cdot\mathbf{r}_l}\int_0^t dt_1 e^{i\Delta_1' t_1}\int_0^{t_1}dt_2 e^{-(\Gamma_{b'}/2)(t_1-t_2)}e^{-i\Delta' t_2}\right]$$
$$\times\left[\frac{\Omega_1\Omega_1' g''}{4}\sum_m e^{i(\Delta\mathbf{k})\cdot\mathbf{r}_m}\int_0^t dt_1 e^{i\Delta' t_1}\int_0^{t_1}dt_2 e^{-(\Gamma_{b'}/2)(t_1-t_2)}e^{i\Delta'' t_2}\int_0^{t_2}dt_3 e^{-(\Gamma_b/2)(t_2-t_3)}e^{-i\Delta t_3}\right] . \quad (34)$$

[The first term corresponds to Fig. 4(b) and the second to Fig. 4(a).] In the calculation of P_{II}, we only keep the terms that give a contribution to phase-matched emission. In particular, this implies that the same atom should be involved in the sums over j and l. We find

$$P_{\text{II}}=-\sum_{\mathbf{k}_1'}8\pi^3\left[\frac{\Omega_1\Omega_1' g''g_1'}{4}\right]^2\sum_{m,j}e^{i(\Delta\mathbf{k})(\mathbf{r}_m-\mathbf{r}_j)}\frac{\delta^{(t)}(\Delta'+\Delta''-\Delta)\delta^{(t)}(\Delta_1'-\Delta')\delta^{(t)}(\Delta_1'+\Delta''-\Delta)}{\left[\left[\frac{\Gamma_b}{2}\right]^2+\Delta^2\right]\left[\left[\frac{\Gamma_{b'}}{2}\right]^2+(\Delta''-\Delta)^2\right]}$$
$$\times\left[\frac{1}{\frac{\Gamma_{b'}}{2}-i\Delta'}+\frac{1}{\frac{\Gamma_{b'}}{2}+i\Delta'}\right] . \quad (35)$$

Using the fact that

$$2\pi\sum_{\mathbf{k}_1'}(g_1')^2\delta^{(t)}(\Delta_1'-\Delta')\delta^{(t)}(\Delta_1'+\Delta''-\Delta)\simeq\Gamma_{b'}\delta^{(t)}(\Delta'+\Delta''-\Delta) \quad (36)$$

and Eq. (28), we obtain

$$\frac{P_{\text{II}}}{t}=-2\pi\left[\frac{\Omega_1\Omega_1' g''}{4}\right]^2\sum_{m,j}e^{i(\Delta\mathbf{k})\cdot(\mathbf{r}_m-\mathbf{r}_j)}\frac{\Gamma_{b'}^2\delta(\omega''+\omega'-\omega)}{\left[\left[\frac{\Gamma_b}{2}\right]^2+\Delta^2\right]\left[\left[\frac{\Gamma_{b'}}{2}\right]^2+\Delta'^2\right]^2} . \quad (37)$$

This term is obviously smaller than P_{I}/t by a factor $(\Gamma_{b'}/\Delta')^2$. Furthermore, a calculation of P_{III}/t done using the same method shows that the phase-matched contribution to P_{III}/t exactly cancels that of P_{II}/t.

3. *Case of collisional damping*

We consider the case of dephasing collisions. These collisions can be described by replacing the atomic Bohr frequencies $\omega_{\alpha\beta}(t)$ by $\omega_{\alpha\beta}(t)+\varphi_{\alpha\beta}(t)$ where $\varphi_{\alpha\beta}(t)$ is the sum of the phase shifts on the α-β transition between time 0 and t. We also define

$$\varphi_{\alpha\beta}(t_2,t_1)=\varphi_{\alpha\beta}(t_2)-\varphi_{\alpha\beta}(t_1) . \quad (38)$$

The average of the phase shifts over all possible collisions gives

$$\langle e^{-i\varphi_{\alpha\beta}(t_2,t_1)}\rangle_{\text{coll}}=e^{-\gamma_{\alpha\beta}(t_2-t_1)} \quad (39)$$

for $t_2>t_1$. When these phase shifts are included in the calculation of $C(n-1,n'+1,\mathbf{k})$, the only difference at the end of the calculation is that $\Gamma_b/2$ and $\Gamma_{b'}/2$, appearing in energy denominators in Eq. (23), are replaced by

$$\Gamma_{ba}=\frac{\Gamma_b}{2}+\gamma_{ba}\ , \tag{40a}$$

$$\Gamma_{b'a}=\frac{\Gamma_{b'}}{2}+\gamma_{b'a}\ . \tag{40b}$$

In the limit where $|\Delta|$ and $|\Delta'|$ are large compared to Γ_{ba} and $\Gamma_{b'a}$, the result given by formulas (27) and (33) is not changed.

Let us now consider the calculation of $P_{\rm II}$. We start from the formula (34) giving $C(n-1,n',\mathbf{k}'',\mathbf{k}'_1)$ and replace the time evolution factors $e^{i\Delta'_1 t_1}$, $e^{i\Delta'' t_2}$, etc., by $e^{i\Delta'_1 t_1}e^{-i\varphi_{b'a}(t_1)}$, $e^{i\Delta'' t_2}e^{-i\varphi_{bb'}(t_2)}$, etc., to include the effect of the phase-interrupting collisions. When calculating $|C(n-1,n',\mathbf{k}'',\mathbf{k}'_1)|^2$, we only keep the terms that contribute to phase-matched emission. These terms can be written as

$$\langle P_{\rm II}\rangle_{\rm coll}=\sum_{m,j} e^{i(\Delta\mathbf{k})\cdot(\mathbf{r}_m-\mathbf{r}_j)}(\langle A_m B_j\rangle_{\rm coll}+{\rm c.c.})\ . \tag{41}$$

The collisions at two different sites m and j being independent, we can separately average A_m and B_j over the collisions ($\langle A_m B_j\rangle_{\rm coll}=\langle A_m\rangle_{\rm coll}\langle B_j\rangle_{\rm coll}$ if $m\neq j$).

The quantity B_j is given by

$$\begin{aligned}B_j=-\sum_{\mathbf{k}'_1}\frac{\Omega_1\Omega'_1}{4}g''g_1'^2\int_0^t dt_1 e^{i\Delta'_1 t_1}e^{-i\varphi_{b'a}(t_1)}
&\times\int_0^{t_1}dt_2 e^{-(\Gamma_{b'}/2)(t_1-t_2)}e^{-i\Delta' t_2}e^{i\varphi_{b'a}(t_2)}\\
&\times\int_0^{t}dt'_1 e^{-i\Delta'_1 t'_1}e^{i\varphi_{b'a}(t'_1)}\\
&\times\int_0^{t'_1}dt'_2 e^{-(\Gamma_{b'}/2)(t'_1-t'_2)}e^{-i\Delta'' t'_2}e^{i\varphi_{bb'}(t'_2)}\int_0^{t'_2}dt'_3 e^{-(\Gamma_b/2)(t'_2-t'_3)}e^{i\Delta t'_3}e^{-i\varphi_{ba}(t'_3)}\ .\end{aligned} \tag{42}$$

This expression can be simplified by using the relation

$$\sum_{\mathbf{k}'_1}(g'_1)^2 e^{i\Delta'_1(t_1-t'_1)}=\Gamma_{b'}\delta(t_1-t'_1)\ , \tag{43}$$

which leads to

$$\begin{aligned}B_j=-\frac{\Omega_1\Omega'_1}{4}g''\Gamma_{b'}\int_0^t dt_1\int_0^{t_1}dt_2 e^{-(\Gamma_{b'}/2)(t_1-t_2)}e^{-i\Delta' t_2}e^{i\varphi_{b'a}(t_2)}&\\
\times\int_0^{t_1}dt'_2 e^{-(\Gamma_{b'}/2)(t_1-t'_2)}e^{-i\Delta'' t'_2}e^{i\varphi_{bb'}(t'_2)}\int_0^{t'_2}dt'_3 e^{-(\Gamma_b/2)(t'_2-t'_3)}e^{i\Delta t'_3}e^{-i\varphi_{ba}(t'_3)}&\ .\end{aligned} \tag{44}$$

We now order the integrals so that the phase shifts appearing under the integral can be written as a sum of $\varphi_{\alpha\beta}(t_i,t_j)$ in nonoverlapping time intervals with $t_i>t_j$. Therefore, we write B_j using (38) as

$$\begin{aligned}B_j=-\frac{\Omega_1\Omega'_1}{4}g''\Gamma_{b'}\Bigg[&\int_0^t dt_1\int_0^{t_1}dt_2 e^{-\Gamma_{b'}(t_1-t_2)}e^{-i\Delta' t_2}\\
&\quad\times\int_0^{t_2}dt'_2 e^{-(\Gamma_{b'}/2)(t_2-t'_2)}e^{-i\Delta'' t'_2}e^{i\varphi_{b'a}(t_2,t'_2)}\int_0^{t'_2}dt'_3 e^{-(\Gamma_b/2)(t'_2-t'_3)}e^{i\Delta t'_3}e^{i\varphi_{ba}(t'_2,t'_3)}\\
&+\int_0^t dt_1\int_0^{t_1}dt'_2 e^{-\Gamma_{b'}(t_1-t'_2)}e^{-i\Delta'' t'_2}\\
&\quad\times\int_0^{t'_2}dt_2 e^{-[(\Gamma_b/2)+(\Gamma_{b'}/2)](t'_2-t_2)}e^{-i\Delta' t_2}e^{i\varphi_{bb'}(t'_2,t_2)}\int_0^{t_2}dt'_3 e^{-(\Gamma_b/2)(t_2-t'_3)}e^{i\Delta t'_3}e^{i\varphi_{ba}(t_2,t'_3)}\\
&+\int_0^t dt_1\int_0^{t_1}dt'_2 e^{-\Gamma_{b'}(t_1-t'_2)}e^{-i\Delta'' t'_2}\int_0^{t'_2}dt'_3 e^{-[(\Gamma_b/2)+(\Gamma_{b'}/2)](t'_2-t'_3)}e^{i\Delta t'_3}e^{i\varphi_{bb'}(t'_2,t'_3)}\\
&\quad\times\int_0^{t'_3}dt_2 e^{-(\Gamma_{b'}/2)(t'_3-t_2)}e^{-i\Delta' t_2}e^{-i\varphi_{b'a}(t'_3,t_2)}\Bigg]\ .\end{aligned} \tag{45}$$

Using Eq. (39) to average over collisions and integrating over time, we obtain

$$\langle B_j\rangle_{\rm coll}=-2\pi\frac{\Omega_1\Omega_1'}{4}g''\frac{\Gamma_{b'}}{\Gamma_{b'}+i(\Delta-\Delta'-\Delta'')}\left[\frac{1}{\Gamma_{ba}^*+i\Delta}\frac{1}{\Gamma_{b'a}^*+i(\Delta-\Delta'')}+\frac{1}{\Gamma_{ba}^*+i\Delta}\frac{1}{\Gamma_{bb'}^*+i(\Delta-\Delta')}+\frac{1}{\Gamma_{b'a}-i\Delta'}\frac{1}{\Gamma_{bb'}^*+i(\Delta-\Delta')}\right]e^{i(\Delta-\Delta'-\Delta'')(t/2)}\delta^{(t)}(\Delta-\Delta'-\Delta'')\ . \tag{46}$$

This expression can be transformed into

$$\langle B_j\rangle_{\rm coll}=-2\pi\frac{\Omega_1\Omega_1'}{4}g''\delta^{(t)}(\Delta-\Delta'-\Delta'')\left[\frac{1}{\Gamma_{ba}^*+i\Delta}\left[\frac{1}{\Gamma_{b'a}^*+i\Delta'}+\frac{1}{\Gamma_{b'a}-i\Delta'}\right]+\frac{(\gamma_{bb'}^a)^*}{(\Gamma_{ba}^*+i\Delta)(\Gamma_{b'a}-i\Delta')(\Gamma_{bb'}^*+i\delta)}\right]e^{i(\Delta-\Delta'-\Delta'')(t/2)}\ . \tag{47}$$

In the absence of collisional damping, the second term in the square brackets disappears ($\gamma_{bb'}^a=0$) and one recovers the same factor found in formula (35). It should be noted that the second term is of order of $|\gamma_{bb'}^a/\Gamma_{bb'}|(1/\Delta^2)$ while the first term is of order $|\Gamma_{b'a}/\Delta|(1/\Delta^2)$. In the presence of collisions and for $|\Delta|,|\Delta'|\gg|\Gamma_{ba}|,|\Gamma_{b'a}|$, the dominant term is the collision-induced one:

$$\langle B_j\rangle_{\rm coll}=-2\pi\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}g''\frac{(\gamma_{bb'}^a)^*}{\Gamma_{bb'}^*+i\delta}\delta^{(t)}(\Delta-\Delta'-\Delta'')e^{i(\Delta-\Delta'-\Delta'')(t/2)}\ . \tag{48}$$

In the limit $|\Delta|,|\Delta'|\gg|\Gamma_{ba}|,|\Gamma_{b'a}|$, the value of $\langle A_m\rangle_{\rm coll}$ is still given by formula (27). Finally, using Eqs. (27), (28), (41), and (48), we obtain

$$\frac{P_{\rm II}}{t}=2\pi\left[\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right]^2\left[\frac{\gamma_{bb'}^a}{\Gamma_{bb'}-i\delta}+\text{c.c.}\right]\left[\sum_{m,j}e^{i\Delta\mathbf{k}\cdot(\mathbf{r}_m-\mathbf{r}_j)}\right]g''^2\delta(\omega''+\omega'-\omega)\ . \tag{49}$$

The procedure used to go from formula (29) to formula (33) can be repeated here and we find

$$\Gamma_{\rm II}=\frac{N^2}{S}\frac{\omega''}{2\varepsilon_0 c\hbar}\left|\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right|^2|d_{bb'}|^2\left[\frac{\gamma_{bb'}^a}{\Gamma_{bb'}-i\delta}+\frac{(\gamma_{bb'}^a)^*}{\Gamma_{bb'}^*+i\delta}\right]\ . \tag{50}$$

One can note that $\Gamma_{\rm II}$ appears to result from the interference between the pair of atoms of quantities of type $\langle A_m\rangle\langle B_j\rangle_{\rm coll}$. It has been shown that $\langle A_m\rangle$ is connected with the usual parametric scattering by atom m, while $\langle B_j\rangle_{\rm coll}$ is associated with collision-aided excitation of level b' of atom j followed by spontaneous emission of a photon ω_1'. These features are well explained by the diagrams of Fig. 4.

The calculation of $\Gamma_{\rm III}$ can be done along the same lines and one finds

$$P_{\rm III}=\sum_{m,j}e^{i\Delta\mathbf{k}\cdot(\mathbf{r}_m-\mathbf{r}_j)}\langle B_m\rangle_{\rm coll}\langle B_j^*\rangle_{\rm coll}\ . \tag{51}$$

The calculation of $P_{\rm III}$ involves an interference between products of terms $\langle B_m\rangle_{\rm coll}$ and $\langle B_j\rangle_{\rm coll}$ relative to atoms m and j. Each of these terms involves a collision and a spontaneous emission of a photon, in agreement with the image of Fig. 5.

Using Eq. (47), in the limit that $|\gamma_{bb'}^a\Delta/\Gamma_{b'a}\Gamma_{bb'}|\gg 1$ and Eqs. (29)–(33), one finally arrives at

$$\Gamma_{\rm III}=\frac{N^2}{S}\frac{\omega''}{2\varepsilon_0 c\hbar}\left|\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right|^2|d_{bb'}|^2\left|\frac{\gamma_{bb'}^a}{\Gamma_{bb'}-i\delta}\right|^2\ . \tag{52}$$

The sum $\Gamma_{\rm I}+\Gamma_{\rm II}+\Gamma_{\rm III}$ where $\Gamma_{\rm I}$, $\Gamma_{\rm II}$, and $\Gamma_{\rm III}$ are given by Eqs. (33), (50), and (52) is obviously equal to the result (9) obtained in the semiclassical approach. There is thus a perfect coherence between the two descriptions. However, the fully quantum description has permitted us to identify the physical origin of the phase-matched emission. The three terms $\Gamma_{\rm I}$, $\Gamma_{\rm II}$, and $\Gamma_{\rm III}$ that appear in the quantum calculation are associated with the interference phenomena described by the diagrams of Figs. 3, 4, and 5, respectively. The calculation presented here is clearly more tedious than the calculation done in the semiclassical approach (or in the Heisenberg approach with quantized fields[11]); however, there are no subtle or basic difficulties. Finally, if the initial state of the field is not a pure state but is described by a density matrix,

$$\rho_F(0)=\sum_n\sum_{n'}P(n)P'(n')|n,n',0\rangle\langle n,n',0|\ , \tag{53}$$

where $P(n)$ and $P'(n')$ are probability distributions centered around n_0 and n_0' with widths Δn and $\Delta n'$ such that $\Delta n\ll n_0$ and $\Delta n'\ll n_0'$, the results (33), (50), and (52) for $\Gamma_{\rm I}$, $\Gamma_{\rm II}$, and $\Gamma_{\rm III}$ remain valid with $\Omega_1=2g\sqrt{n_0}$ and $\Omega_1'=2g'\sqrt{n_0'}$.

CONCLUSION

We have presented in this paper a theory of the pressure-induced extra resonances in four-wave mixing (PIER 4) using quantized fields in the Schrödinger representation. Even if the calculations are more complicated than those done previously with classical fields[3] or with the quantized field in the Heisenberg representation,[11] our approach leads to a clear picture of the physical origin of the PIER 4 resonances. We believe that our explanation allows one to answer the questions generally asked about PIER 4 (origin of the phase-matching condition, conservation of photon number, constructive role played by the relaxation mechanism). Our interpretation of multiwave mixing in terms of interference between scattering amplitudes by different atoms shows also that this process and the extra resonances do not require temporally coherent fields. All these effects can be observed with pure number states for the field and do not involve the creation of a macroscopic dipole moment in the sample. Moreover, the Schrödinger approach allows us to see certain correlations which are hidden in the Heisenberg approach. For example, it should be clear from Figs. 4 and 5 that the pressure-induced resonance is always correlated with the emission of photons having frequencies different from ω, ω', or ω'', in contrast with the parametric process of Fig. 3. In addition, the gain for field ω' associated with the parametric process of Fig. 3 does not persist for the collision-induced resonance.

In conclusion, we have offered yet another interpretation of the pressure-induced resonances. We hope that this interpretation adds some additional insight as to the physical origin of the resonances.

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APPENDIX A: DESCRIPTION OF PIER 4 IN THE DRESSED-ATOM BASIS

The aim of this appendix is to show how the pressure-induced extra resonances in four-wave mixing appear in the dressed-state basis, and in particular, how they are related to the Raman coherences for a single atom that have been considered previously.[6,9,11]

1. Case of negligible collisional damping

We denote by $|A_1,\ldots,A_j,\ldots A_N;\ n,n',0\rangle$ the dressed eigenstate of H_0 that tends towards $|a_1,\ldots,a_j,\ldots,a_N;\ n,n',0\rangle$ when g and g' tend towards 0. Let us write the perturbation expansion of this state:

$$|A_1,\ldots,A_j,\ldots,A_N;n,n',0\rangle=|a_1,\ldots,a_j,\ldots,a_N;n,n',0\rangle+\frac{\Omega_1}{2\Delta}\sum_j e^{i\phi_j}|a_1,\ldots,b_j,\ldots,a_N;n-1,n',0\rangle$$
$$+\frac{\Omega_1'}{2\Delta'}\sum_j e^{i\phi_j'}|a_1,\ldots,b_j',\ldots,a_N;n,n'-1,0\rangle\ . \qquad \text{(A1)}$$

Similarly, we denote by

$$|A_1,\ldots,B_j,\ldots,A_N;n,n',0\rangle,\quad |A_1,\ldots,B_j',\ldots,A_N;n,n',0\rangle,\quad |A_1,\ldots,B_j,\ldots,B_l',\ldots,A_N;n,n',0\rangle$$

the eigenstates of H_0 that tend towards

$$|a_1,\ldots,b_j,\ldots,a_N;n,n',\rangle,\quad |a_1,\ldots,b_j',\ldots,a_N;n,n',0\rangle,\quad |a_1,\ldots,b_j,\ldots,b_l',\ldots,a_N;n,n',0\rangle$$

when g and g' tend towards 0.

Let us assume first that the system is initially in the state

$$|\psi(0)\rangle=|A_1,\ldots,A_j,\ldots,A_N;n,n',0\rangle \qquad \text{(A2)}$$

and calculate the probability to have a photon emitted in the mode $(\omega'',\mathbf{k}'')$. This probability is proportional to $|\mathcal{S}|^2$ where

$$\mathcal{S}=\langle A_1,\ldots,A_j,\ldots,A_N;n-1,n'+1,\mathbf{k}''|V''|A_1,\ldots,A_j,\ldots,A_N;n,n',0\rangle \qquad \text{(A3)}$$

and V'' is given by Eq. (18).

This coupling involves the annihilation of one ω photon and the creation of one photon each in modes ω' and ω'', in agreement with the scheme of Fig. 2. Using (18), (25), and (A1), we find

$$\frac{\mathcal{S}}{\hbar}=\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}g''\sum_j e^{i(\Delta\mathbf{k})\cdot\mathbf{r}_j} . \tag{A4}$$

The probability of spontaneous emission that is proportional to $|\mathcal{S}|^2$ grows as N^2 in the phase-matched direction. Even if the physical conditions differ from those considered in the case of Dicke supperradiance,[13] the parametric emission of a photon ω'' shares several properties of the superradiance. For example, the two processes correspond to a spontaneous-emission rate proportional to N^2. In some sense, one can consider the parametric emission of a photon ω'' as a superradiant emission in the dressed-state basis.

A quantitative estimate of the rate of spontaneous emission can be done using the Fermi golden rule. The calculation is identical to the one that starts from formula (30) and leads to the value (33) for $\Gamma_{\rm I}$.

2. Case of collisional damping

The preceding discussions have shown that the emission in the phase-matched direction arises from the interference between the emission of different atoms. To describe the phenomena, we need at least two atoms. These atoms will be labeled j and l. We look for the term having a dependence $e^{i\Delta\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_l)}$ in the probability of emission of a photon $(\omega'',\mathbf{k}'')$. The initial density matrix for the total system "atoms + field" is

$$\rho(0)=|A_j,A_l;n,n',0\rangle\langle A_j,A_l;n,n',0| , \tag{A5}$$

and we also assume for the sake of simplicity that $\delta=0$. To second order in the incident fields, the component that is proportional to $e^{i(\Delta\mathbf{k})\cdot(\mathbf{r}_j-\mathbf{r}_l)}$ in the probability of emission of a photon $\omega'',\mathbf{k}''$ is

$$\left[\frac{d\Gamma}{d\Omega''}\right]=\frac{2\pi}{\hbar}\rho(\hbar\omega'')[(A_{jl}+B_{jl}+B_{lj}^*+C_{jl})] , \tag{A6}$$

with

$$\begin{aligned}A_{jl}=&\langle A_j,A_l;n-1,n'+1,\mathbf{k}''|V_j''|A_j,A_l;n,n',0\rangle\\ &\times\langle A_j,A_l;n,n',0|\rho|A_j,A_l;n,n',0\rangle\\ &\times\langle A_j,A_l;n,n',0|V_l''|A_j,A_l;n-1,n'+1,k''\rangle ,\end{aligned} \tag{A7}$$

$$\begin{aligned}B_{jl}=&\langle B_j',A_l;n-1,n',\mathbf{k}''|V_j''|B_j,A_l;n-1,n',0\rangle\\ &\times\langle B_j,A_l;n-1,n',0|\rho|B_j'A_l;n,n'-1,0\rangle\\ &\times\langle B_j',A_l;n,n'-1,0|V_l''|B_j',A_l;n-1,n',\mathbf{k}''\rangle ,\end{aligned} \tag{A8}$$

$$\begin{aligned}C_{jl}=&\langle B_j',B_l';n-1,n'-1,\mathbf{k}''|V_j''|B_j,B_l';n-1,n'-1,0\rangle\\ &\times\langle B_j,B_l';n-1,n'-1,0|\rho|B_j',B_l;n-1,n'-1,0\rangle\\ &\times\langle B_j',B_l;n-1,n'-1,0|V_l''|B_j',B_l';n-1,n'-1,\mathbf{k}''\rangle ,\end{aligned} \tag{A9}$$

where V_j'' means that we consider only the contribution of atom j to V''. The calculations of the density matrix elements that appear in formulas (A8) and (A9) have been derived previously:[6,9]

$$\langle B_j,A_l;n-1,n',0|\rho|B_j',A_l;n,n'-1,0\rangle=\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\frac{\gamma_{bb'}^a}{\Gamma_{bb'}}e^{i(\phi_j-\phi_j')} , \tag{A10a}$$

$$\langle B_j,B_l';n-1,n'-1,0|\rho|B_j',B_l;n-1,n'-1,0\rangle=\left[\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right]^2\left|\frac{\gamma_{bb'}^a}{\Gamma_{bb'}}\right|^2 e^{i(\phi_j-\phi_j'-\phi_l+\phi_l')} . \tag{A10b}$$

These two dressed-atom coherences have a nonvanishing value only in presence of collisional damping ($\gamma_{bb'}^a\neq 0$). Using (A5), (A6), and (A7), one finds again $\Gamma_{\rm I}$. Using (A6), (A8), and (A10a) one obtains $\Gamma_{\rm II}$; and from (A6), (A9), and (A10b) one finds $\Gamma_{\rm III}$. Thus the dressed-atom basis also allows one to deduce the rate of emission. The new terms that arise in the presence of collisional damping are associated with Raman coherences between dressed states[5,11] and are obviously related to the diagrams shown in Figs. 4 and 5. Formula (A8) corresponds to the situation of Fig. 4, where a parametric mixing for atom l interferes with a collisionally aided excitation for atom j. Formula (A9) corresponds to the situation of Fig. 5 where two symmetric collisionally aided excitations of atoms j and l are involved and produce an interference in the emission of a ω'' photon.

APPENDIX B: DESCRIPTION OF THE RELAXATION BY THE INTERACTION WITH A BATH

In this appendix, we describe the relaxation mechanism by the interaction with a bath with quantum numbers $\mu,\nu,\ldots$. The motivation of this appendix is twofold. First, extra resonances can be triggered by relaxation mechanisms different from collisions[17,22] and the approach given here can be applied to other mechanisms. Second, the possibility to follow the quantum numbers of the bath during the interaction allows us to strengthen the physical interpretation given in Sec. II.

We assume that each atom interacts with a separate bath. The quantum numbers for the bath in contact with atom j are labeled $\mu_j,\nu_j,\ldots$. We assume that all the baths are identical: they have the same Hamiltonian, the same interaction Hamiltonian with the atom, and the same density matrix

$$\rho_{b_j}=\sum_\mu p(\mu)|\mu_j\rangle\langle\mu_j| . \tag{B1}$$

The new unperturbed Hamiltonian H_0' is now

$$H_0'=H_0+H_b+H_{lb} , \tag{B2}$$

where H_0 is given by formula (16), H_b is the Hamiltonian of the bath

$$H_b=\sum_j H_{b_j} , \tag{B3}$$

and H_{Ib} is the interaction between the atoms and the baths

$$H_{Ib}=\sum_j H_{Ib_j} \ . \tag{B4}$$

As discussed previously, the physics can be understood by considering a set of two atoms, j and l. We thus limit the following discussion to these two atoms. The eigenstates of H_0+H_b are $|A_j,A_l;n,n',0;\mu_j,\nu_l\rangle$, $|B_j,A_l;n-1,n',0;\mu_j',\nu_l\rangle$, etc. By analogy with what occurs in the case of collisions, we take the following matrix elements for H_{Ib}:

$$\langle B_j,A_l;n-1,n',0;\mu_j',\nu_l'|H_{Ib_j}|A_j,A_l;n,n',0;\mu_j,\nu_l\rangle =\delta_{\nu_l'\nu_l}\frac{\Omega_1}{2\Delta}e^{i\phi_j}W_{BA}^{\mu'\mu} \ , \tag{B5a}$$

$$\langle B_j',A_l;n,n'-1,0;\mu_j'',\nu_l''|H_{Ib_j}|A_j,A_l;n,n',0;\mu_j,\nu_l\rangle =\delta_{\nu_l'',\nu_l}\frac{\Omega_1'}{2\Delta'}e^{i\phi_j'}W_{B'A}^{\mu''\mu} \ . \tag{B5b}$$

We assume that the system is initially in the state $|A_j,A_l;n,n',0;\mu_j,\nu_l\rangle$ and we look for the probability of having the two atoms excited at a later time, one atom being in the B state, the other in the B' state. We have thus to calculate the following matrix element of the evolution operator $U(t,0)$:

$$C_{B_jB_l'}^{\mu_j'\nu_l'}=\langle B_j,B_l';n-1,n'-1,0;\mu_j',\nu_l'|U(t,0)|A_j,A_l;n,n',0;\mu_j,\nu_l\rangle \ . \tag{B6}$$

Using perturbation theory to second order, we obtain

$$C_{B_jB_l'}^{\mu_j'\nu_l'}=-\frac{1}{\hbar^2}\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}e^{i(\phi_j+\phi_l')}W_{BA}^{\mu'\mu}W_{B'A}^{\nu'\nu}\left[\int_0^t dt_1\int_0^t dt_2\Theta(t_1-t_2)e^{i(\omega_{\mu'\mu}-\Delta)t_1}e^{i(\omega_{\nu'\nu}-\Delta')t_2} +\int_0^t dt_1\int_0^t dt_2\Theta(t_1-t_2)e^{i(\omega_{\nu'\nu}-\Delta')t_1}e^{i(\omega_{\mu'\mu}-\Delta)t_2}\right] , \tag{B7}$$

where $\Theta(\tau)$ is the Heaviside function $[\Theta(\tau)=1$ if $\tau>0$ and $\theta(\tau)=0$ if $\tau<0]$. By exchanging t_1 and t_2 in the second integral we find

$$C_{B_jB_l'}^{\mu_j'\nu_l'}=-\frac{1}{\hbar^2}\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}e^{i(\phi_j+\phi_l')}W_{BA}^{\mu'\mu}W_{B'A}^{\nu'\nu}\int_0^t dt_1 e^{i(\omega_{\mu'\mu}-\Delta)t_1}\int_0^t dt_2 e^{i(\omega_{\nu'\nu}-\Delta')t_2} \ . \tag{B8}$$

The component $|\psi_{BB'}\rangle$ of the state vector for which one atom is in the B state, the other atom being in the B' state, is thus

$$|\psi_{BB'}\rangle=\sum_{\mu',\nu'}C_{B_jB_l'}^{\mu_j'\nu_l'}e^{-i(\omega_{\mu'\mu}+\omega_{\nu'\nu})t}|B_j,B_l';n-1,n'-1,0;\mu_j',\nu_l'\rangle +\sum_{\mu'',\nu''}C_{B_j'B_l}^{\mu_j''\nu_l''}e^{-i(\omega_{\mu''\mu}+\omega_{\nu''\nu})t}|B_j',B_l;n-1,n'-1,0;\mu_j'',\nu_l''\rangle \ . \tag{B9}$$

The probability that one photon is emitted in the mode $(\omega'',\mathbf{k}'')$ is proportional to

$$P=\sum_{\mu''',\nu'''}\left|\left\langle B_j',B_l';n-1,n'-1,\mathbf{k}'';\mu_j''',\nu_l'''\left|\frac{V''}{\hbar}\right|\psi_{BB'}\right\rangle\right|^2 , \tag{B10}$$

where V'' is given by formula (18). We only retain in the calculation of P the interference term $P_{\rm int}$ which leads to the phase-matched emission,

$$P_{\rm int}=(g'')^2\left[\sum_{\mu',\nu'}C_{B_jB_l'}^{\mu_j'\nu_l'}(C_{B_j'B_l}^{\mu_j'\nu_l'})^*e^{-i\mathbf{k}''\cdot(\mathbf{r}_j-\mathbf{r}_l)}+\text{c.c.}\right] . \tag{B11}$$

Using (B8), we obtain

$$P_{\rm int}=\frac{(g'')^2}{\hbar^4}\left[\frac{\Omega_1\Omega_1'}{4\Delta\Delta'}\right]^2\left[\sum_{\mu',\nu'}W_{BA}^{\mu'\mu}(W_{B'A}^{\mu'\mu})^*(W_{BA}^{\nu'\nu})^*W_{B'A}^{\nu'\nu}e^{i(\Delta\mathbf{k})\cdot(\mathbf{r}_j-\mathbf{r}_l)} \times\int_0^t dt_1 e^{i(\omega_{\mu'\mu}-\Delta)t_1}\int_0^t dt_1' e^{-i(\omega_{\mu'\mu}-\Delta')t_1'}\int_0^t dt_2 e^{i(\omega_{\nu'\nu}-\Delta')t_2}\int_0^t dt_2' e^{-i(\omega_{\nu'\nu}-\Delta)t_2}+\text{c.c.}\right] . \tag{B12}$$

Finally, we have to average the formula (75) using the density matrix of the bath

$$\bar{P}_{\text{int}} = \sum_{\mu,\nu} p(\mu)p(\nu)P_{\text{int}} \ . \tag{B13}$$

Since the bath has a very dense energy spectrum, the function

$$g^{A}_{BB'}(\tau) = \frac{1}{\hbar^2} \sum_{\mu,\mu'} p(\mu) W^{\mu'\mu}_{BA} (W^{\mu'\mu}_{B'A})^* e^{i\omega_{\mu'\mu}\tau} \tag{B14}$$

has a very short correlation time. If we define

$$\gamma^{A}_{BB'} = \int d\tau \, g^{A}_{BB'}(\tau) \ , \tag{B15}$$

it follows that

$$\bar{P}_{\text{int}} \simeq (g'')^2 \left[\frac{\Omega_1 \Omega'_1}{4\Delta\Delta'} \right]^2 |\gamma^{A}_{BB'}|^2 \frac{\sin^2(\delta t/2)}{(\delta/2)^2} \times (e^{i(\Delta \mathbf{k})\cdot(\mathbf{r}_j - \mathbf{r}_l)} + \text{c.c.}) \tag{B16}$$

This result shares most of the properties of the contribution Γ_{III} [see Eq. (52)] to PIER 4. It leads to a cooperative spontaneous emission in the direction where the phase-matching condition is fulfilled. It exhibits a resonance around $\delta=0$ and it requires a relaxation mechanism to induce transfers from A to B and B' ($\gamma^{A}_{BB'} \neq 0$).

When atom j absorbs a photon ω, the quantum number of its bath changes from μ to μ'. In particular, this transition of the bath is necessary to absorb the energy mismatch $\hbar\Delta$. When atom j absorbs a photon ω', the quantum number of its bath changes from μ to μ''. However, in order to have an interference term such as the one of formula (B11) we need to have $\mu''=\mu'$. The quantum number of the bath should be the same at the end of the process, independently of the atom (j or l) that has absorbed the photon ω and emitted the photon ω''. The scheme of the process is similar to all the interference phenomena. There are two possible paths to go from $|A_j, A_l; n, n', 0; \mu_j, \nu_l\rangle$ to $|B'_j, B'_l; n-1, n'-1, \mathbf{k}''; \mu'_j, \nu'_l\rangle$: the first path is through $|B_j, B'_l; n-1, n'-1, 0; \mu'_j, \nu'_l\rangle$; the second path is through $|B'_j, B_l; n-1, n'-1, 0; \mu'_j, \nu'_l\rangle$.

A similar picture can be used to find the term Γ_{II}. In that case also there are two possible paths to go from $|A_j, A_l; n, n', 0; \mu_j, \nu_l\rangle$ to $|A_j, B'_l; n-1, n', \mathbf{k}''; \mu_j, \nu'_l\rangle$. The first path is through $|A_j, A_l; n-1, n'+1, \mathbf{k}''; \mu_j, \nu_l\rangle$; the second path is through $|A_j, B_l; n-1, n', 0; \mu_j, \nu'_l\rangle$.

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