LINE SHIFTS IN COOPERATIVE SPONTANEOUS EMISSION

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Cooperative spontaneous emission, such as observed in photon echo experiments, is proved to be frequency shifted by a measurable amount with respect to the atomic transition frequency. The theory presented here is based on a renormalization procedure which rules out unobservable contributions.

In this letter we report a line shift effect associated with cooperative spontaneous emission, i.e. that due to a many-atom system prepared in a state with non-zero atom-atom correlations. Atom-atom correlations due to the common radiation field have been considered since the early years of the quantum theory [1] †, yet within the harmonic oscillator approximation. A suitable representation for collective states of this kind has been introduced by Dicke [3], who has shown by an first order perturbative approach that the spontaneous emission rate for some of these states can be markedly different from that of a system of uncorrelated atoms. Use of Weisskopf-Wigner theory [4] in a radiation damping problems leads to an exponential decay with a decay constant equal to the rate given by the first order calculation. Intrinsically associated with the damping is also a level shift, which is normally neglected for two reasons. The first is the poor operational meaning of level shift. By this we mean that whenever we measure the frequency of a spontaneously emitted line, the emitting atom is already dressed by the electromagnetic interaction and the only way to speak of a level shift is by referring to the bare atomic levels calculated by a suitable model. Only when there exists a fortunate combination of two bare atomic states with equal energy, which are then affected differently by the electromagnetic interaction, can one measure a shift. This is the case with the Lamb shift between the 2s and $2p_{1/2}$ levels of the hydrogen atom [5]. The second reason is that, while the damping rate is specified at the resonance frequency by an energy conservation requirement, the level shift implies an integration over all frequencies. In a nonrelativistic treatment such an integral diverges unless one introduces a suitable cut-off. Even so, the calculation can lead to wrong results unless one subtracts those contributions which are already built in the theory, as the electromagnetic electron mass in the Lamb shift (mass renormalization [6]).

We show in this letter that:

(i) A level shift in cooperative spontaneous emission does have an operational meaning. Indeed, it can be measured as the frequency difference between the spontaneous radiation from a correlated atomic state and that from an isolated atom, and it can be calculated since a cut-off is provided by the very nature of the coherent state.

(ii) The spontaneous radiation field is generated by many sequential decays from the prepared collective state through intermediate states down to the ground state. Although the bare collective system is

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† Ref. [1], besides reviewing the previous works on the correlations broadening and shift of a fluorescent line (Kopplungsbreite) presents a new elegant treatment, based on the use of the Lorentz-Lorenz formula. More modern formulations of the same problem have appeared in recent years, and reviewed in ref. [2].

made of equidistant energy levels [3], the level shifts associated with successive decays are by no means equal to one another. This is due to the peculiar nature of the sequential decay, which cannot be described by the successive application of the usual Weisskopf-Wigner theory but requires more rigorous considerations [7] *.

The hamiltonian of a system of N two-level atoms interacting with a quantized radiation field is

$$H = \hbar\,(K+V),$$

$$K = \tfrac{1}{2}\omega_0 \sum_{j=1}^{N} \sigma_j^3 + \sum_{\boldsymbol{k}} \omega_{\boldsymbol{k}}\, a_{\boldsymbol{k}}^{\dagger}\, a_{\boldsymbol{k}}\ ; \tag{1}$$

$$V = \sum_{j,\boldsymbol{k}} g_{\boldsymbol{k}} \{[\exp \mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}_j - \omega_k t)]\,(\sigma_j^+ - \sigma_j^-)\,a_{\boldsymbol{k}} + [\exp -\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}_j - \omega_k t)]\,(\sigma_j^+ - \sigma_j^-)\,a_{\boldsymbol{k}}^{\dagger}\}.$$

Here the σ_j denote the Pauli operators acting on the atom at the position $\boldsymbol{x}_j$, $a_{\boldsymbol{k}}^{\dagger}$, $a_{\boldsymbol{k}}$ are the $\boldsymbol{k}$th mode photon creation and annihilation operators, and ω_0, ω_k represent respectively the atomic transition frequency (measured in a single atom experiment) and the kth electromagnetic mode eigenfrequency. We have used periodic boundary conditions over a volume τ for the field, and the sum over $\boldsymbol{k}$ is to be taken over all modes and polarizations. The interaction strength in MKS units is $g_{\boldsymbol{k}} = \mathrm{i}\omega_0\, \wp_{\boldsymbol{k}} (2\epsilon_0 \hbar\omega_k \tau)^{-1/2}$ where ϵ_0 is the dielectric constant of the vacuum and $\wp_{\boldsymbol{k}}$ is the matrix element of the projection of the electric dipole operator $e\,\boldsymbol{r}$ on the $\boldsymbol{k}$th polarization vector, taken between the two atomic states. We have used for the interaction potential the form ** $(e/m)\,\boldsymbol{A}\cdot\boldsymbol{p}$ and we retain both "real" ($\sigma^+ a$ and $\sigma^- a^{\dagger}$) and "virtual" ($\sigma^+ a^{\dagger}$ and $\sigma^- a$) terms in V.

The decay process can be conveniently described by means of a resolvent operator $G(z)$, which is defined in terms of the evolution operator $U(t)$ as [10]

$$U(t) = (1/2\pi\mathrm{i}) \int_{\mathcal{C}} \mathrm{d}z\; e^{-\mathrm{i}zt}\, G(z), \tag{2}$$

$$G(z) = [z - (K+V)]^{-1}\ , \tag{3}$$

$\mathcal{C}$ being a contour that runs from $+\infty$ to $-\infty$ above the singularities of $G(z)$ on the complex plane. We first consider a system of N atoms confined in a region of linear size smaller than the wavelength $\lambda_0 = 2\pi c/\omega_0$ of the atomic transition. We may thus drop the phase factors $\exp \pm \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}_j$ appearing in the interaction hamiltonian. We specify the atomic states in the representation of the eigenstates of the total angular momentum ***, denoting them by the corresponding quantum numbers r, called cooperation number [3], ($\frac{1}{2}N \geqslant r \geqslant 0$, $\frac{1}{2}$) and $m (r \geqslant m \geqslant -r)$. Let us assume that the system is prepared in an initial state consisting of the vacuum state of the field plus an atomic state with the maximum cooperation number $r = \frac{1}{2}N$, and an m number equal to m_0. Since in this case the hamiltonian conserves the total angular momentum, the atomic system decays to its ground state $|r = \frac{1}{2}N, m = -\frac{1}{2}N\rangle$ through a

* A possible level shift associated with cooperative spontaneous emission was considered first by Fain [8]. However his treatment differs from ours for the following reasons: i) He uses a perturbative approach, while we employ a non-perturbative treatment by summing over an infinite set of relevant diagrams. ii) Fain's level shift refers to the transition between two *unstable* states. No real experiment can be designed to pick up such a transition, and the only thing which can be observed is the evolution toward the final *stable* state.

** The hamiltonian $(e/m)\,\boldsymbol{A}\cdot\boldsymbol{p}$ can be replaced by $e\,\boldsymbol{E}\cdot\boldsymbol{r}$ leading to the same result, see ref. [9]. As far as the A^2 term is concerned, it is immediately seen that it does not contribute to the level shift, since it is cancelled by the renormalization.

*** We have introduced the σ_j earlier as operators on the individual atom energy eigenstates $|\uparrow\rangle_j$ (excited) and $|\downarrow\rangle_j$ (ground):

$$\sigma^3 \begin{Bmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{Bmatrix} = \pm\tfrac{1}{2} \begin{Bmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{Bmatrix}, \quad \sigma^{\pm}\,|\uparrow\rangle = \begin{Bmatrix} 0 \\ |\downarrow\rangle \end{Bmatrix}, \quad \sigma^{\pm}\,|\downarrow\rangle = \begin{Bmatrix} |\uparrow\rangle \\ 0 \end{Bmatrix}.$$

We have made use of the isomorphism of any two-state system to a spin system. Since H now contains only $\Sigma_j \sigma_j^{\pm} = S^{\pm}$ we have $[H, S^2] = 0$. Therefore we use the basis $|r, m\rangle$ for atomic states:

$$S\cdot S\,|r,m\rangle = r(r+1)\,|r,m\rangle\ ,\ S^3\,|r,m\rangle = m\,|r,m\rangle\ ,$$

$$S^{\pm}|r,m\rangle = \{(r \mp m)\,(r \pm m + 1)\}^{1/2}\,|r, m \pm 1\rangle\ .$$

ladder of intermediate levels with equal r. We assume that the electromagnetic cavity in which the sample is radiating is large enough, so that the number of modes around the transition frequency is much larger than the number of atoms. In such a way we may consider only the case where no more than one photon is emitted into each mode.

The unperturbed eigenstates of the system are $|m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0-m}\rangle$ where $\boldsymbol{k}_1, \ldots, \boldsymbol{k}_{m_0-m}$ is the set of photons emitted in the first m_0-m decays, and $|m_0; \phi\rangle$ is the initial state. We then introduce the projection operators Λ_m and P_m defined as follows

$$\Lambda_m = \sum_{\boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0-m}} |m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0-m}\rangle\langle m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0-m}| \,, \tag{4a}$$

$$P_m = 1 - \sum_{j=m}^{m_0} \Lambda_j \,. \tag{4b}$$

The quantity of interest is clearly the projection of the resolvent $G(z)$ between the final ground state and the initial state. That quantity is given by [7]

$$\langle -r; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0}| G(z) |m_0; \phi\rangle$$

$$= \langle -r; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0}| F^{(-r)} \prod_{m=-r}^{m_0-1} (F_m + 1) |m_0; \phi\rangle \langle m_0; \phi| [z - K - \mathcal{R}^{(m_0)}]^{-1} |m_0; \phi\rangle \tag{5a}$$

where $F^{(m)}$, F_m, and $\mathcal{R}^{(m)}$ are given respectively by

$$F^{(m)} = 1 + [z - K]^{-1} P_m V F^{(m)} \,, \tag{5b}$$

$$F_m = [z - K - \mathcal{R}^{(m)}]^{-1} \Lambda_m V F^{(m)} \,, \tag{5c}$$

$$\mathcal{R}^{(m)} = \Lambda_m V F^{(m)} \Lambda_m \,. \tag{5d}$$

Eqs. (5) are rigorous. In applying this result to our sequential decay we make the following approximations.

(i) We confine our attention to transitions that go through the resonant states, that is, neglect the "one" terms appearing in eq. (5a). The error involved in this neglect can be shown [7] to be of the order of the (very small) ratio of the resonant width to the typical atomic transition frequency ω_0.

(ii) We neglect the rescattering of radiation once emitted. This amounts to diagonalizing the $\mathcal{R}^{(j)}$, requiring that terms in them representing virtual transitions such as

$$|m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0-m_0}\rangle \rightarrow |m-1; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0-m_0}, \boldsymbol{k}\rangle$$
$$\rightarrow |m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{j-1}, \boldsymbol{k}_{j+1}, \ldots, \boldsymbol{k}_{m_0-m}, \boldsymbol{k}\rangle$$

be suppressed. This is a good approximation due to the fact that the lifetime of the decaying state is much longer than the flight time of radiation through our sample size, as was shown in detail elsewhere [7]. We may thus regard eq. (5d) as the vacuum expectation value of the operator $VF^{(m)}$ with respect to the emitted radiation, i.e. the self energy of the jth intermediate state. It then follows from eqs. (1) to (5) that the evolution of the initial state toward a final state $|-r; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0}\rangle$ is described by

$$|-r; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0}| U(t) |m_0; \phi\rangle$$

$$= (1/2\pi i) \int_{\mathcal{C}} dz \, e^{-izt} [z - K_{-r}]^{-1} \prod_{m=-r+1}^{m_0} [z - K_m - \Sigma_m(z)]^{-1} \, M_{m-1, m}(k) \,. \tag{6}$$

Here K_m is the energy eigenvalue of the mth state (in frequency units);

$$M_{m-1,m}(k) = [i\omega_0 \wp/(3\epsilon_0 \hbar c k \tau)^{1/2}][(r-m)(r+m+1)]^{1/2} \tag{7}$$

represents the transition matrix element between two adjacent levels averaged over the solid angle ($\wp$ being the maximum value of $\wp_k$) and Σ_m stands for the self energy of the mth state. It should be noted at this point that Σ_m can in general be expressed as an explicit function of all Σ_q with $q < m$ by the repeated use of eq. (5b) in eq. (5c). Since the analysis is tedious, we relegate it to the main paper to be published elsewhere and confine our treatment of Σ_m to the second order in V. We may then write

$$\Sigma_m(z) = \langle m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0} | V\{1 + (z-K)^{-1} P_m V\} | m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0} \rangle . \tag{8}$$

We now turn to the evaluation of these self energy expressions. Upon using eqs. (1) and (4b) in eq. (8), replacing the sum over photon states associated with P_m by an integral and approximating the argument z by the unperturbed eigenvalue, i.e. $z = K_m$ we obtain

$$\Sigma_m = \Delta\Omega_m - i\gamma_m \tag{9}$$

Here

$$\gamma_m = (r+m)(r-m+1)[8\pi^2 \wp^2/3\lambda_0^3 \epsilon_0 \hbar] = (r+m)(r-m+1)\gamma_s \tag{10}$$

is the decay constant, γ_s being the decay rate of an isolated atom, and

$$\Delta\Omega_m = [\tau/c(2\pi)^3]\{\int d^3k |\langle m-1; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0 - m+1} | V | m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0 - m}\rangle|^2 (k_0 - k)^{-1}$$
$$+ \int d^3k |\langle m+1; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0 - m+1} | V | m; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{m_0 - m}\rangle|^2 (k_0 + k)^{-1}\} \tag{11}$$

is the total level shift arising from the principal part integration of the resonant transition plus the contribution due to the virtual transitions. In evaluating this integral it is convenient to divide the range of integration into two intervals by introducing a value k_c of the order of the reciprocal size 2 of the cooperating region ($k_c \, 2\pi/l$). In the first interval where k varies from zero to k_c the matrix element obeys the selection rule for a point-like sample ($\Delta r = 0$, $\Delta m = \pm 1$) and hence it is given by eq. (7). In the second interval in which the corresponding wavelengths are comparable with, or less than, the interatomic distance, the atoms can be regarded as independent of one another, and hence the matrix element averaged over random atomic positions reduces to that of a single atom. Let us now apply our renormalization procedure by subtracting the level shift contribution associated with a single atom. In the first interval, this latter contribution is of order of $(1/N)$ compared to the former one, and can be neglected. In the second interval there is an exact cancellation between the two contributions. Therefore our level shift calculation will consist in evaluating all integrals up to the cut-off frequency $\omega_c = ck_c$.

Thus we obtain

$$\Delta\Omega_m = -\{4\wp^2/(3\lambda_0^2 \hbar \epsilon_0)[\int_0^{k_c} dk\, k(r+m)(r-m+1)(k-k_0)^{-1} + \int_0^{k_c} dk\, k(r-m)(r+m+1)(k+k_0)^{-1}]$$

$$\approx -\pi^{-1} \gamma_m (\lambda_0/l)[1 + \{(r-m)(r+m+1)/(r+m)(r-m+1)\}]. \tag{12}$$

Upon inserting eq. (9) into (6), performing the contour integrations, and summing over all the possible permutation π among mode indices we find the joint probability for the emission of the frequencies $\omega_1 \cdots \omega_{r+m}$, viz,

$$W_{r+m_0}(\omega_1, \omega_2, \ldots \omega_{r+m_0}) = \lim_{t \to \infty} |\sum_{\pi} \langle -r; \boldsymbol{k}_1, \boldsymbol{k}_2, \ldots, \boldsymbol{k}_{r+m_0} | U(t) | m_0; \phi\rangle|^2 \tag{13}$$

The lineshape $P(\omega)$ we can be obtained by integrating the above joint distribution over $r + m_0 - 1$ variables. The interesting role played by the interference terms on shaping the spectral profile of the sequential decay was discussed elsewhere [11]. The center frequency of the emitted radiation is only due to the diagonal elements of eq. (1) which follows from energy conservation. It is given by

$$\langle\omega\rangle = \int d\omega_1 d\omega_2 \ldots d\omega_{r+m_0}\, \omega W(\omega_1, \ldots, \omega_{r+m_0})$$

$$= \omega_0 - \{ \sum_{j=1}^{r+m_0} (\Delta\Omega_j - \Delta\Omega_{j-1}) \} / (r+m_0) = \omega_0 - \{ \Delta\Omega_{m_0} / (r+m_0) \} \ . \tag{14}$$

Thus, the cooperative level shift $\Delta\omega = \langle\omega\rangle - \omega_0$ is given by the mean value of the dressed frequency spectrum of these sequential decays minus the atomic transition frequency. Comparing the level shift $\Delta\omega$ with the cooperative damping rate γ_c [1], we see that their ratio is given by

$$\Delta\omega/\gamma_c \approx \lambda_0/l \ . \tag{15}$$

The state of the maximum cooperation number, viz. $r = \frac{1}{2} N$ can be prepared by pumping the system in its ground state by a $\pi/2$ plane wave electromagnetic pulse followed by a π pulse (photon echo experiment [12]) and can be shown to be a packet of Dicke states. The maximum cooperative level shift is given by

$$\Delta\omega_{max} \approx \gamma_c(\lambda_0) \ , \tag{16}$$

where $\gamma_c(\lambda_0)$ denotes the cooperative decay associated with all the atoms contained in a volume of order λ_0^3. For example, for the 6943 Å transition of ruby with 0.05% Cr^{3+} we have $\rho \approx 1.6 \times 10^{19}$ cm^{-3}, $\lambda_0^3 \approx 0.4 \times 10^{-12}$ cm^3, $N(\lambda_0) \approx 10^6$, and hence $\gamma_c(\lambda_0) \approx 3 \times 10^8$ sec^{-1}; for the 5841 Å transition of ionized argon at the usual conditions of laser operation we have $\rho \approx 10^{14}$ cm^{-3}, $\lambda_0^3 \approx 0.2 \times 10^{-12}$ cm^3, $N(\lambda_0) \approx 20$, and $\gamma_c(\lambda_0) \approx 8 \times 10^9$ sec^{-1}. The effect described here seems to be observable. However, our calculation was done without taking into account other interactions (atomic or phonon collisisons, Doppler broadening, etc.) which could mask in some cases the above effect.

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REFERENCES

[1] V. Weisskopf, Physik. Z. 3 (1933) 1.
[2] F. T. Arecchi, G. L. Masserini and P. Schwendimann, Riv. Nuovo Cimento 1 (1969) 181.
[3] R. H. Dicke, Phys. Rev. 93 (1954) 99.
[4] V. Weisskopf and E. Wigner, Z. Physik, 63 (1930) 54.
[5] W. E. Lamb, Jr. and R. C. Retherford, Phys. Rev. 79 (1950) 549.
[6] H. A. Bethe, Phys. Rev. 72 (1947) 339.
[7] A. S. Goldhaber and K. M. Watson, Phys. Rev. 160 (1967) 1151;
L. Mower, Phys. Rev. 165 (1968) 145.
[8] V. M. Fain, Soviet Phys. JETP 36 (1959) 798.
[9] E. A. Powers, Introductory quantum electrodynamics (Longmans, London, 1964) sec. 9.2.
[10] A. Messiah, Quantum mechanics, Vol. II (Wiley, New York, 1962);
M. L. Goldberger and K. M. Watson, Collision theory (Wiley, New York, 1964).
[11] F. T. Arecchi, D. M. Kim and I. W. Smith, Nuovo Cimento Letters 3 (1970) 598.
[12] I. D. Abella, N. A. Kurnit and S. R. Hartmann, Phys. Rev. 141 (1966) 391.