Quantum interferences and the question of thermodynamic equilibrium

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We derive from first principles the dynamical equations for the interaction between a heat bath and a multilevel atom with some near degenerate states. Such dynamical equations exhibit atomic coherence terms which arise from the interference of transition amplitudes. We address the question whether such equations lead to a steady state that is consistent with the thermodynamic equilibrium. We show that coherence affects the dynamics of the system, but the equilibrium conditions are still characterized by Boltzmann factors. We also show how an asymmetric treatment of spontaneous and stimulated processes could lead to a steady state which is at variance with the principles of thermodynamic equilibrium. We show that such a steady state can be realized by pumping with broadband laser fields. Finally, we show that coherences in the dynamical equations can be probed via the spectrum of fluorescence.

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I. INTRODUCTION

It is well known that quantum coherences can be produced by pumping a system with coherent fields—an outstanding example being the phenomenon of coherent population trapping [1]. It is also well understood how quantum coherence can be created in interactions involving a common bath with a set of closely lying states [2–12]. These types of coherences have led to very remarkable phenomena like lasing without population inversion [4], etc. One would like to understand the role of coherences if the bath is at a finite temperature. At the outset one would not expect any coherences if the system is in thermodynamic equilibrium as the density matrix has the form $\exp(-\beta H)$, which is clearly diagonal in a basis in which H is diagonal. However, a microscopic derivation of the master equation for a system interacting with a heat bath does show the appearance of coherence terms in dynamical equations. Clearly, one needs to demonstrate the consistency of the dynamical equation with thermodynamic equilibrium. This then raises a very interesting question: what could then be the observational consequence of such coherence terms in the master equation? The present paper deals with such aspects. We derive from first principles the dynamical equation, which exhibits coherences, and which we show to be consistent with thermodynamic equilibrium. We give several examples of physical quantities that can be used to study the effect of coherences in the dynamical equations.

The organization of the paper is as follows. In Sec. II we derive the basic equations of motion for our model and show the possibility of atomic coherence due to interaction with a bath. In Sec. III we show how *thermodynamic equilibrium is achieved* in a steady state even in the presence of such coherence terms in the master equation. In Sec. IV we show how the coherence terms in the master equation can be probed through the emission spectrum. We also demonstrate how an *asymmetric* treatment of spontaneous vs stimulated emission can lead to a steady state which is at variance with thermodynamic equilibrium. In Sec. V we demonstrate how such situations can be realized by pumping with a broadband laser.

II. EQUATIONS OF MOTION

We consider a collection of three-level atoms, the excited levels $|1\rangle$, $|2\rangle$, and ground level $|3\rangle$ (V system) in a bath of thermal field (Fig. 1). The Hamiltonian for this system will be

$$H = H_0 + H_{AR}, \tag{1}$$

where

$$H_0 = \hbar\omega_{13}A_{11} + \hbar\omega_{23}A_{22} + \sum_{ks} \hbar\omega_{ks}a_{ks}^{\dagger}a_{ks},$$

$$H_{AR} = -\sum_{ks} \{(g_{ks}A_{13} + f_{ks}A_{23})(a_{ks} + a_{ks}^{\dagger}) + \text{H.c.}\}.$$

Here $A_{lm} = |l\rangle\langle m|$ and $\hbar\omega_{lm}$ is the energy separation between the levels $|l\rangle$ and $|m\rangle$. The annihilation (creation) operator corresponding to the radiation field in the mode ks is

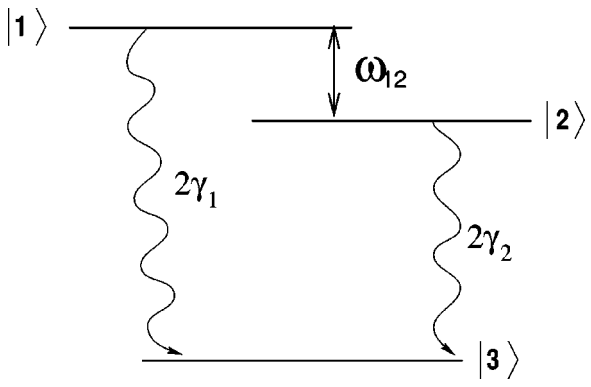

FIG. 1. Schematic of a V system in a thermal bath. The γ's denote the spontaneous emission rates and the excited levels are assumed to be coupled via the vacuum field.

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a_{ks} $(a_{ks}^{\dagger})$. The coupling constants are $g_{ks}=i\sqrt{(2\pi ck/\hbar L^3)}\vec{d}_{13}\cdot\hat{\epsilon}_{ks}$ and $f_{ks}=i\sqrt{(2\pi ck/\hbar L^3)}\vec{d}_{23}\cdot\hat{\epsilon}_{ks}$ where $\vec{d}_{j3}$ is the dipole matrix element for the transition $|j\rangle\leftrightarrow|3\rangle$ $(j=1,2)$ and $\hat{\epsilon}_{ks}$ is the unit polarization vector. L^3 is the quantization volume which finally will be extended to infinity. The above Hamiltonian in the interaction picture will be

$$H_I=-\sum_{ks}\left[\{g_{ks}A_{13}e^{i\omega_{13}t}+f_{ks}A_{23}e^{i\omega_{23}t}\}a_{ks}e^{-i\omega_{ks}t}+\text{H.c.}\right], \tag{2}$$

where we drop the antiresonant terms (rotating wave approximation). We study the dynamics of this system in the master equation framework [2]. The master equation derived in the Born and Markov approximation reads as

$$\begin{aligned}\frac{\partial\rho}{\partial t}=&-i[\omega_{13}A_{11}+\omega_{23}A_{23},\rho]-\Gamma_1[A_{11}\rho-A_{33}\rho_{11}]\\&-\Gamma_2[A_{22}\rho-A_{33}\rho_{22}]-\Gamma_2\alpha\cos\theta[A_{12}\rho-A_{33}\rho_{21}]\\&-\frac{\Gamma_1\cos\theta}{\alpha}[A_{21}\rho-A_{33}\rho_{12}]-\gamma_1N_1[A_{33}\rho-A_{11}\rho_{33}]\\&-\gamma_2N_2[A_{33}\rho-A_{22}\rho_{33}]+\left(\frac{\gamma_1N_1}{\alpha}+\gamma_2N_2\alpha\right)\\&\times\cos\theta A_{21}\rho_{33}+\text{H.c.}\end{aligned} \tag{3}$$

Here $2\gamma_j=4|\vec{d}_{j3}|^2\omega_{j3}^3/3\hbar c^3$ is the natural linewidth of the level $|j\rangle$ which occurs due to the zero point fluctuation of the electromagnetic field, $N_j=(\exp[\beta\hbar\omega_{j3}]-1)^{-1}$ is the mean number of thermal photons on the transition $|j\rangle\leftrightarrow|3\rangle$ at temperature T $(\beta=1/kT)$, and $\Gamma_j=\gamma_j(N_j+1)$ $(j=1,2)$. θ is the angle between the matrix elements $\vec{d}_{13},\vec{d}_{23}$ and $\alpha=|\vec{d}_{13}|/|\vec{d}_{23}|$. Note that the above master equation was derived without any assumption about the orientation of dipole matrix elements. The $\cos\theta$ terms in the above equation are the cross (interference) terms in addition to the direct decay terms. They are particularly important when $\omega_{12}\approx\Gamma_1,\Gamma_2$, and arise due to the two transitions $|1\rangle\leftrightarrow|3\rangle$ and $|2\rangle\leftrightarrow|3\rangle$ coupling with the same vacuum. If $\omega_{12}\gg\Gamma_1,\Gamma_2$ then we can neglect such interference terms under the secular approximation. The present discussion is based on situations where such nonsecular terms are important. In recent times, such terms have been much in focus because they create atomic coherence without any coherent field [5–13], although in other situations [14,15] external fields have been used to create a similar effect. The equations of motion for the various density matrix elements in the Schrödinger picture are

$$\dot{\rho}_{11}=-2\Gamma_1\rho_{11}+2\gamma_1N_1\rho_{33}-\Gamma_2\alpha\cos\theta(\rho_{12}+\rho_{21}), \tag{4a}$$

$$\dot{\rho}_{22}=-2\Gamma_2\rho_{22}+2\gamma_2N_2\rho_{33}-\frac{\Gamma_1\cos\theta}{\alpha}(\rho_{12}+\rho_{21}), \tag{4b}$$

$$\begin{aligned}\dot{\rho}_{12}=&-[\Gamma_1+\Gamma_2+i\omega_{12}]\rho_{12}-\frac{\Gamma_1\cos\theta}{\alpha}\rho_{11}\\&-\Gamma_2\alpha\cos\theta\rho_{22}+\left(\gamma_2\alpha N_2+\frac{\gamma_1N_1}{\alpha}\right)\cos\theta\rho_{33},\end{aligned} \tag{4c}$$

$$\dot{\rho}_{13}=-[\Gamma_1+\gamma_2N_2+\gamma_1N_1+i\omega_{13}]\rho_{13}-\Gamma_2\alpha\cos\theta\rho_{23}, \tag{4d}$$

$$\dot{\rho}_{23}=-[\Gamma_2+\gamma_1N_1+\gamma_2N_2+i\omega_{23}]\rho_{23}-\frac{\Gamma_1\cos\theta}{\alpha}\rho_{13}. \tag{4e}$$

Traditionally one has the rate equations for populations and coherences as simple decay. However, now the dynamics of the coherence ρ_{12} is coupled with the diagonal elements and vice versa. The crucial question is: *Does this system evolve into a thermodynamic equilibrium even in the presence of such coherences in the density matrix equations?*

III. STEADY STATE BEHAVIOR

We evaluate the steady state for the set of equations (4). After tedious calculation we arrive at the following simplified result:

$$\rho_{11}=\frac{\Gamma_2\gamma_1N_1}{(\Gamma_1\Gamma_2+\Gamma_2\gamma_1N_1+\Gamma_1\gamma_2N_2)},$$

$$\rho_{22}=\frac{\Gamma_1\gamma_2N_2}{(\Gamma_1\Gamma_2+\Gamma_2\gamma_1N_1+\Gamma_1\gamma_2N_2)}. \tag{5}$$

The remaining elements are zero. A clear demonstration of thermodynamic equilibrium can be seen by taking the ratio of populations,

$$\frac{\rho_{11}}{\rho_{22}}=\frac{\exp[-\beta\hbar\omega_{13}]}{\exp[-\beta\hbar\omega_{23}]}, \tag{6}$$

which is in accordance with the Boltzmann distribution. Note that one arrives at the same set of results (5) even in the absence of interference terms. This essentially means that, although the system may evolve in a different way, in steady state the thermodynamic equilibrium is obtained even in the presence of coherence terms in the master equation. (We show in the Appendix that this result is true in general for a multilevel atom in a thermal bath in the presence of interference terms.) To show that the steady state conditions are the same both in the presence and in the absence of interference, we measure the entropy of the system. The entropy is defined as

$$S(t)=-\sum_{i=1}^{3}\Lambda_i\ln\Lambda_i, \tag{7}$$

where the Λ_i's are the eigenvalues of the density matrix ρ. At $t=0$ we have $\rho_{33}(0)=1$, which is a pure state and the entropy will be zero. To numerically evaluate the entropy we

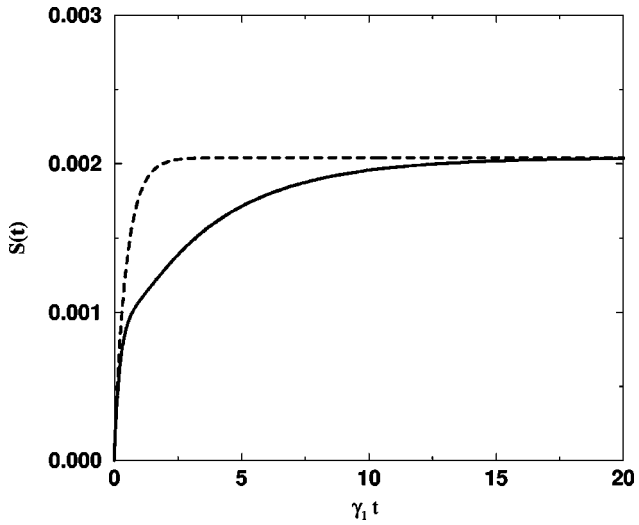

FIG. 2. The dynamical evolution of entropy. The parameters are $\gamma_1=\gamma_2=\omega_{12}$, $N_1=N_2=10^{-5}$, and $\alpha=1$. The solid line is in the presence of interference ($\theta=0°$) and the dashed curve is in the absence ($\theta=90°$). In both cases the long time behaviors are the same.

make the canonical transformation of $\rho_{j3}\equiv\bar{\rho}_{j3}\exp[-i(\omega_{13}+\omega_{23})t/2]$ $(j=1,2)$ in Eqs. (4). Note in Fig. 2 that in both the presence and absence of interference, the system evolves to the same value of entropy. We have also verified that the time derivative of entropy continuously decreases. Note that the time taken to reach the equilibrium value is greater in the presence of interference. This happens because the interference terms pump the system back to excited levels, and thus the populations decay with an effective lifetime that is more than the lifetime in the absence of interference. We note here that the analysis of Savchenko *et al.* [10] based on Green's functions seems to imply the existence of coherence under equilibrium conditions. We have shown above that, although nondiagonal elements are present in the equations for populations, they do not contribute in steady state.

An exception to the above occurs for the degenerate case $\omega_{12}=0$, which is ambiguous when $\theta=0°$. A unique straightforward steady state solution of Eqs. (4) does not exist. In fact, ρ_{11} and ρ_{22} remain arbitrary. This situation arises because there exists a constant of motion in this case [2]. Consider the states

$$|-\rangle=\frac{|\vec{d}_{23}||1\rangle-|\vec{d}_{13}||2\rangle}{d},\quad |+\rangle=\frac{|\vec{d}_{13}||1\rangle+|\vec{d}_{23}||2\rangle}{d}, \tag{8}$$

where $d^2=|\vec{d}_{13}|^2+|\vec{d}_{23}|^2$. It is easy to see that $\rho_{--}=K$ where K is a constant. In general the steady state solution is given by

$$\rho_{11}=\rho_{22}=\frac{N(1+K)+K}{2(1+2N)},\quad \rho_{12}=\frac{N(1-3K)-K}{2(1+2N)},$$
$$0\leqslant K\leqslant 1, \tag{9}$$

where $N_1=N_2=N$. Clearly, a unique steady state solution exists for a given value of K. The above result may seem to violate equilibrium conditions, but it is not surprising as the state $|-\rangle$ is *decoupled* from the bath. Thus if we initially start from $K=1$ then the system always remains in $|-\rangle$. The state $|-\rangle$ is an example of a trapped state [1] and is very much of current interest in the context of quantum computing using decoherence free subspace [16]. However, there are other situations where the steady state could be different from the one determined by thermodynamic equilibrium. An example is given below.

Asymmetric treatment of spontaneous vs stimulated processes

The decays Γ_1,Γ_2 contain the contribution of both spontaneous (γ_1,γ_2) and stimulated $(\gamma_1N_1,\gamma_2N_2)$ emission processes. Thus interference also exists in both these processes. If we include a parameter a for interference in stimulated emission and b for interference in spontaneous emission, the master equation in this case will be

$$\frac{\partial\rho}{\partial t}=-i[\omega_{13}A_{11}+\omega_{23}A_{22},\rho]-\Gamma_1[A_{11}\rho-A_{33}\rho_{11}]-\Gamma_2[A_{22}\rho-A_{33}\rho_{22}]-\gamma_2(aN_1+b)\alpha\cos\theta[A_{12}\rho-A_{33}\rho_{21}]$$
$$-\frac{\gamma_1(aN_1+b)\cos\theta}{\alpha}[A_{21}\rho-A_{33}\rho_{12}]-\gamma_1N_1[A_{33}\rho-A_{11}\rho_{33}]-\gamma_2N_2[A_{33}\rho-A_{22}\rho_{33}]$$
$$+a\left(\frac{\gamma_1N_1}{\alpha}+\gamma_2N_2\alpha\right)\cos\theta A_{21}\rho_{33}+\text{H.c.} \tag{10}$$

It implies that $a=0,b=1$ would mean interference only in the spontaneous process and $a=1,b=0$ would mean interference only in the stimulated process. Such a segregation is not just theoretical; we will show later that there are other kinds of bath where such conditions can be realized. However, for a thermal field, a correct physical situation would imply either $a=b=1$ or $a=b=0$. It turns out that the neglect of any one interference term (a or b) results in a steady state, which is at variance with thermal equilibrium. We found the following steady state when $a=0,b=1$:

$$\rho_{11}=\frac{[(\Gamma_1+\Gamma_2)^2+\omega_{12}^2]\Gamma_2\gamma_1N_1+\gamma_2\cos^2\theta(\Gamma_1+\Gamma_2)(\gamma_2^2\alpha^2N_2-\gamma_1^2N_1)}{D_1}, \tag{11a}$$

$$\rho_{22}=\frac{[(\Gamma_1+\Gamma_2)^2+\omega_{12}^2]\Gamma_1\gamma_2N_2+\gamma_1\cos^2\theta(\Gamma_1+\Gamma_2)(\gamma_1^2N_1/\alpha^2-\gamma_2^2N_2)}{D_1}, \tag{11b}$$

$$\rho_{12}=\frac{-(\Gamma_1+\Gamma_2-i\omega_{12})(\Gamma_1\gamma_2^2N_2\alpha+\Gamma_2\gamma_1^2N_1/\alpha)\cos\theta}{D_1}, \tag{11c}$$

where

$$D_1=\left\{[(\Gamma_1+\Gamma_2)^2+\omega_{12}^2](\Gamma_1\Gamma_2+\Gamma_2\gamma_1N_1+\Gamma_1\gamma_2N_2)-\gamma_1\gamma_2\cos^2\theta(\Gamma_1+\Gamma_2)^2-(\Gamma_1+\Gamma_2)\cos^2\theta(\gamma_2\alpha^2-\gamma_1)\left(\frac{\gamma_1^2N_1}{\alpha^2}-\gamma_2^2N_2\right)\right\}.$$

When $a=1,b=0$ we find

$$\rho_{11}=\frac{[(\Gamma_1+\Gamma_2)^2+\omega_{12}^2]\Gamma_2\gamma_1N_1-\gamma_1N_1\gamma_2N_2\cos^2\theta(\Gamma_1+\Gamma_2)(\Gamma_2+\gamma_1N_1+\gamma_2^2\alpha^2N_2/\gamma_1N_1)}{D_2}, \tag{12a}$$

$$\rho_{22}=\frac{[(\Gamma_1+\Gamma_2)^2+\omega_{12}^2]\Gamma_1\gamma_2N_2-\gamma_1N_1\gamma_2N_2(\Gamma_1+\Gamma_2)\cos^2\theta(\Gamma_1+\gamma_2N_2+\gamma_1^2N_1/\alpha^2\gamma_2N_2)}{D_2}, \tag{12b}$$

$$\rho_{12}=\frac{(\Gamma_1+\Gamma_2-i\omega_{12})(\Gamma_2\gamma_1^2N_1/\alpha+\Gamma_1\gamma_2^2N_2\alpha)\cos\theta}{D_2}, \tag{12c}$$

where

$$D_2=\left\{[(\Gamma_1+\Gamma_2)^2+\omega_{12}^2](\Gamma_1\Gamma_2+\Gamma_1\gamma_2N_2+\Gamma_2\gamma_1N_1)-(\Gamma_1+\Gamma_2)\gamma_1N_1\gamma_2N_2\left(2\Gamma_1+2\Gamma_2+\gamma_1N_1+\gamma_2N_2+\frac{\gamma_1^2N_1}{\gamma_2N_2\alpha^2}+\frac{\gamma_2^2\alpha^2N_2}{\gamma_1N_1}\right)\cos^2\theta\right\}.$$

In both the cases the *steady state coherence* among excited levels is *nonzero*. In Fig. 3 we show the dynamics of $|\rho_{12}|$ for various values of a and b. We take the initial state as $|3\rangle$. Thus, for $a=b=0$, $\rho_{12}(t)=0$. As seen in Fig. 3, for $a=b=1$ the *steady state coherence is absent*. In the case of an asymmetric treatment, equilibrium conditions are violated.

We now explain why thermodynamic equilibrium does not permit such an asymmetric treatment. We note that the emission (absorption) processes are determined by the antinormally ordered (normally ordered) correlation functions of the electromagnetic field. In thermodynamic equilibrium both these correlations are connected via the *fluctuation-dissipation* theorem and therefore both stimulated and spontaneous processes are to be treated on the same footing. In order to treat them asymmetrically one needs extra freedom and we show in Sec. V that pumping by broadband lasers provides such a freedom.

IV. EMISSION SPECTRUM: A PROBE OF COHERENCE TERMS IN THE MASTER EQUATION

In the preceding section we showed that the long time effect of coherence on atomic variables is absent. In this section we show the effect of coherence on the emitted radiation. We derive the emission spectrum and show the existence of a dark line as a result of atomic coherence via decay terms.

All the nine elements of ρ can be written in a compact matrix equation as

$$\frac{\partial\Psi}{\partial t}=M\Psi, \tag{13}$$

where

$$\Psi^\dagger=[\rho_{11},\ \rho_{12},\ \rho_{13},\ \rho_{21},\ \rho_{22},\ \rho_{23},\ \rho_{31},\ \rho_{32},\ \rho_{33}], \tag{14}$$

and M is a 9×9 matrix corresponding to the coefficients of ρ in Eq. (4). The positive frequency part of the radiated electric field at a distance $\vec{r}$ in the far field region is given by

$$\vec{E}^+(\vec{r},t)=-\frac{\omega_{13}^2}{c^2r}[\hat{r}\times\hat{r}\times\vec{d}_{13}]A_{31}(t)e^{-ikr}-\frac{\omega_{23}^2}{c^2r}[\hat{r}\times\hat{r}\times\vec{d}_{23}]A_{32}(t)e^{-ikr}. \tag{15}$$

The emission spectrum is given by

$$\mathcal{S}(\omega)=\lim_{t\to\infty}\int_0^\infty \mathrm{Re}\{\exp(-i\omega\tau)\langle E^-(t+\tau)\cdot\vec{E}^+(t)\rangle\}d\tau, \tag{16}$$

and the two-time field correlation is

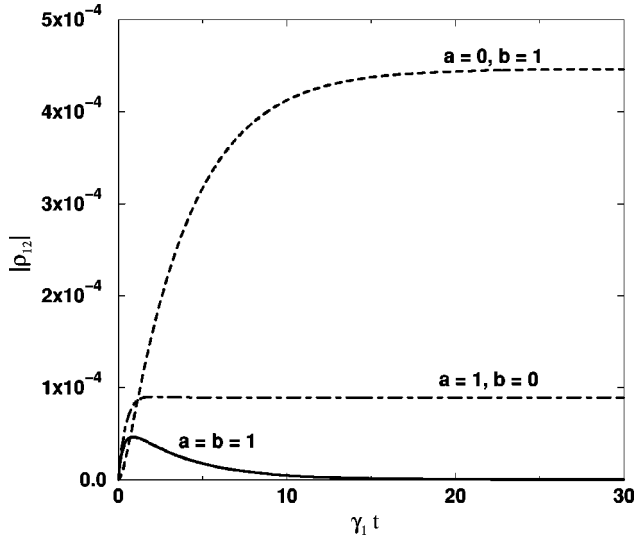

FIG. 3. Plotted are the absolute values of coherence ρ_{12} as a function of time. The parameters are as in Fig. 2.

$$\langle \vec{E}^{-}(\vec{r},t+\tau)\cdot E^{+}(\vec{r},t)\rangle = \frac{\omega_{13}^4|\vec{d}_{13}|^2\sin^2\phi_1}{c^4r^2}\langle A_{13}(t+\tau)A_{31}(t)\rangle + \frac{\omega_{23}^4|\vec{d}_{23}|^2\sin^2\phi_2}{c^4r^2}\langle A_{23}(t+\tau)A_{32}(t)\rangle + \frac{\omega_{23}^2\omega_{13}^2|\vec{d}_{23}||\vec{d}_{13}|}{c^4r^2}(\cos\theta-\cos\phi_1\cos\phi_2) \times\{\langle A_{23}(t+\tau)A_{31}(t)\rangle+\langle A_{13}(t+\tau)A_{32}(t)\rangle\}. \tag{17}$$

Here ϕ_1,ϕ_2 are the angles between $\vec{r}$ and $\vec{d}_{13},\vec{d}_{23}$, respectively. From Eq (13) we can write

$$\Psi(t+\tau)=L(\tau)\Psi(t) \tag{18}$$

where the matrix $L(\tau)=\exp(M\tau)$ and the elements of $\Psi(t)$ are given in Eq. (14). Using Eq. (18) and the regression theorem we find the two-time correlation functions in the limit $t\to\infty$ as

$$\langle A_{13}(t+\tau)A_{31}(t)\rangle = L_{77}(\tau)\rho_{11}(\infty),$$

$$\langle A_{13}(t+\tau)A_{32}(t)\rangle = L_{78}(\tau)\rho_{22}(\infty),$$

$$\langle A_{23}(t+\tau)A_{32}(t)\rangle = L_{88}(\tau)\rho_{22}(\infty),$$

$$\langle A_{23}(t+\tau)A_{31}(t)\rangle = L_{87}(\tau)\rho_{11}(\infty).$$

The elements of matrix L required for the above expression are given by $L_{77}(\tau)=\rho_{31}(\tau)$, $L_{87}(\tau)=\rho_{32}(\tau)$, solved with the initial condition $\rho_{31}(0)=1$, and $L_{88}(\tau)=\rho_{32}(\tau)$, $L_{87}(\tau)=\rho_{31}(\tau)$, with the initial condition $\rho_{32}(0)=1$. Taking the one-sided Fourier transform we get

$$L_{77}(\omega)=\frac{[\Gamma_2+\gamma_1N_1+\gamma_2N_2-i(\delta-\omega_{12}/2)]}{D_3}, \tag{19a}$$

$$L_{78}(\omega)=\frac{-\Gamma_2\alpha\cos\theta}{D_3}, \tag{19b}$$

$$L_{88}(\omega)=\frac{[\Gamma_1+\gamma_1N_1+\gamma_2N_2-i(\delta+\omega_{12}/2)]}{D_3}, \tag{19c}$$

$$L_{87}(\omega)=\frac{-\Gamma_1\cos\theta/\alpha}{D_3}, \tag{19d}$$

where

$$D_3=[\Gamma_1+\gamma_1N_1+\gamma_2N_2-i(\delta+\omega_{12}/2)] \times[\Gamma_2+\gamma_1N_1+\gamma_2N_2-i(\delta-\omega_{12}/2)]-\Gamma_1\Gamma_2\cos^2\theta,$$

and $\delta=(\omega_{13}+\omega_{23})/2-\omega$.

The final expression for the spectrum is

$$\mathcal{S}(\omega)=\mathrm{Re}\left[\frac{\omega_{13}^4|\vec{d}_{13}|^2}{c^4r^2}\sin^2\phi_1L_{77}(\omega)\rho_{11}+\frac{\omega_{23}^4|\vec{d}_{23}|^2}{c^4r^2} \times\sin^2\phi_2L_{88}(\omega)\rho_{22}+\frac{\omega_{13}^2\omega_{23}^2|\vec{d}_{13}||\vec{d}_{23}|}{c^4r^2} \times(\cos\theta-\cos\phi_1\cos\phi_2)\{L_{78}(\omega)\rho_{22}+L_{87}(\omega)\rho_{11}\}\right]. \tag{20}$$

Here the ρ's denote the steady state value. The first two terms above denote the emission from the two excited levels and the last term is due to interference. If we take the ratio $\omega_{13}/\omega_{23}\approx1$ and assume that the difference $\Gamma_1-\Gamma_2$ is negligible, the spectrum can be written in a simpler form as a sum of Lorentzian and dispersive contributions as

$$\mathcal{S}(\omega)/C=\frac{[\gamma_1(2\omega_0-\omega_{12})\rho_{11}+\gamma_2(2\omega_0+\omega_{12})\rho_{22}]}{4\omega_0}\left[\frac{\gamma_0}{(\delta+\omega_0)^2+\gamma_0^2}\right]+\frac{[\gamma_1(2\omega_0+\omega_{12})\rho_{11}+\gamma_2(2\omega_0-\omega_{12})\rho_{22}]}{4\omega_0} \times\left[\frac{\gamma_0}{(\delta-\omega_0)^2+\gamma_0^2}\right]+\frac{(\Gamma_1\gamma_2\rho_{11}+\Gamma_2\gamma_1\rho_{22})\cos^2\theta}{2\omega_0}\left[\frac{\delta-\omega_0}{(\delta-\omega_0)^2+\gamma_0^2}-\frac{\delta+\omega_0}{(\delta+\omega_0)^2+\gamma_0^2}\right], \tag{21}$$

where we take $\phi_1=\phi_2=\pi/2$. Here $\gamma_0=(\Gamma_1+\Gamma_2)/2+\gamma_1N_1+\gamma_2N_2$, $\omega_0=\sqrt{(\omega_{12}^2-4\Gamma_1\Gamma_2\cos^2\theta)}/2$, and $C=3\hbar\omega_{13}/2cr^2$. The above result (21) is valid for $\omega_{12}>2\sqrt{\Gamma_1\Gamma_2}\cos\theta$. Note that the interference terms appear as dispersive contributions, which is a general feature observed among such interference effects [17]. A deviation from this behavior can be seen in certain cases as observed here when $\omega_{12}<2\sqrt{\Gamma_1\Gamma_2}\cos\theta$. The spectrum in this case will be

$$\mathcal{S}(\omega)/C=\frac{[\gamma'\gamma_1\rho_{11}+\gamma'\gamma_2\rho_{22}+(\Gamma_1\gamma_2\rho_{11}+\Gamma_2\gamma_1\rho_{22})\cos^2\theta]}{2\gamma'}\left[\frac{\gamma_0+\gamma'}{\delta^2+(\gamma_0+\gamma')^2}\right]$$
$$+\frac{[\gamma'\gamma_1\rho_{11}+\gamma'\gamma_2\rho_{22}-(\Gamma_1\gamma_2\rho_{11}+\Gamma_2\gamma_1\rho_{22})\cos^2\theta]}{2\gamma'}\left[\frac{\gamma_0-\gamma'}{\delta^2+(\gamma_0-\gamma')^2}\right]$$
$$+\frac{(\gamma_2\rho_{22}-\gamma_1\rho_{11})\omega_{12}}{4\gamma'}\left[\frac{\delta}{\delta^2+(\gamma_0-\gamma')^2}-\frac{\delta}{(\delta^2+(\gamma_0+\gamma')^2}\right], \tag{22}$$

where we have written $\omega_0=i\gamma'$. Here even the interference terms appear as Lorentzian. In both cases the contribution of interference is a sharp dip in the spectrum at the averaged frequency of the two excited levels. Thus in the presence of interference the two levels can be resolved even when the two excited levels have separation much less than their linewidth. We show the spectrum both in the presence and in the absence of interference in Fig. 4. The dark line (at $\delta=0$) in the spectrum is the observational effect of interference which arises for the system in thermodynamic equilibrium. For $\gamma_1=\gamma_2=\gamma$, $N_1=N_2=N$ at $\delta=0$ the spectrum is proportional to

$$\mathcal{S}(\omega)/C=\frac{4\gamma^2N^2}{(1+3N)(\gamma_0^2+\omega_0^2)}, \tag{23}$$

when $\theta=0°$. Thus the observation of a dark line at $\delta=0$ depends on N. The smaller the value of N, the better will be the observed interference effect.

V. REPLACEMENT OF THERMAL BATH BY A BROADBAND PUMPING LASER

We have shown earlier that an asymmetric treatment of spontaneous emission and stimulated emission could lead to a variety of different steady states. However, this is not valid for interaction with a thermal bath. We now show that there are other types of bath where such situations could be realized in practice. Consider, for example, pumping by a broadband pumping laser, where the field is given by

$$\vec{E}(t)=\varepsilon(t)\hat{\varepsilon}e^{-i\omega_1t}+\text{c.c.}, \tag{24}$$

and the field amplitude is δ correlated, $\langle\varepsilon(t)\varepsilon^*(t-\tau)\rangle=2R\delta(\tau)$. Below we show two cases that correspond to $a=1, b=0$ and $a=0, b=1$ as in Sec. III.

Case I: a = 1, b = 0. As discussed in Sec. III this would correspond to no interference in spontaneous emission, while interference in stimulated process persists. For this we consider the dipole matrix elements as orthogonal ($\vec{d}_{23}\perp\vec{d}_{13}$). We take a single broadband field, polarized along $\hat{\epsilon}_1$, which makes an angle Φ_1 with $\vec{d}_{13}$, and the central frequency tuned midway between the two excited levels. The master equation for such a bath in the Schrödinger picture can be derived as

$$\frac{\partial\rho}{\partial t}=-i[\omega_{13}A_{11}+\omega_{23}A_{22},\rho]-(\gamma_1+p_1)[A_{11}\rho-A_{33}\rho_{11}]$$
$$-(\gamma_2+p_2)[A_{22}\rho-A_{33}\rho_{22}]-\sqrt{p_1p_2}[A_{12}\rho+A_{21}\rho$$
$$-A_{33}\rho_{12}-A_{33}\rho_{21}]-p_1[A_{33}\rho-A_{11}\rho_{33}]$$
$$-p_2[A_{33}\rho-A_{22}\rho_{33}]+2\sqrt{p_1p_2}A_{21}\rho_{33}+\text{H. c.}, \tag{25}$$

where $2p_j=2R|\vec{d}_{j3}\cdot\hat{\epsilon}_1|^2/\hbar^2$ $(j=1,2)$ is the radiative broadening due to the pumping field. For simplicity we have taken the dipole matrix elements as real. Note from Eq. (25) that interference terms here correspond to $\sqrt{p_1p_2}$. This coherence arises due to a polarized broadband field coupling to both the transitions. The coherence will be important for separation ω_{12} less than the spectral width of the pumping field [18]. Here the interference in spontaneous emission is absent.

Case II: a = 0, b = 1. This would correspond to a situation where interference in stimulated emission is absent, but interference in spontaneous emission is present. Consider a situation where the dipole matrix elements are at an angle θ where $\theta\neq0,\pi/2$. Both the transitions are now pumped by two different broadband fields of the same central frequency ω_1 but different polarizations $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ such that $\vec{d}_{23}\cdot\hat{\epsilon}_1=0$ and $\vec{d}_{13}\cdot\hat{\epsilon}_2=0$ [19]. This would imply that we have two different pumping strengths along the two arms of the V system given by $2p_j=2R|\vec{d}_{j3}\cdot\hat{\epsilon}_j|^2/\hbar^2$ $(j=1,2)$. Further, if the pumping fields $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ are uncorrelated then the master equation will be

$$\frac{\partial\rho}{\partial t}=-i[\omega_{13}A_{11}+\omega_{23}A_{22},\rho]-(\gamma_1+p_1)[A_{11}\rho-A_{33}\rho_{11}]$$
$$-(\gamma_2+p_2)[A_{22}\rho-A_{33}\rho_{22}]-\sqrt{\gamma_1\gamma_2}\cos\theta[A_{12}\rho+A_{21}\rho$$
$$-A_{33}\rho_{12}-A_{33}\rho_{21}]-p_1[A_{33}\rho-A_{11}\rho_{33}]$$
$$-p_2[A_{33}\rho-A_{22}\rho_{33}]+\text{H. c.}, \tag{26}$$

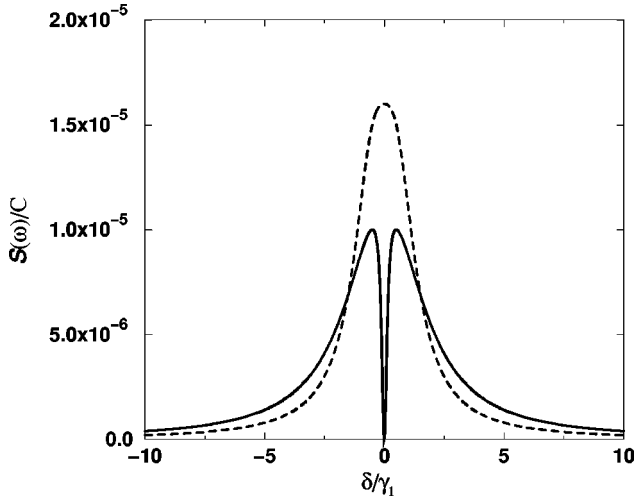

FIG. 4. The emission spectrum is plotted in dimensionless units. The parameters are $\gamma_1=\gamma_2$, $\omega_{12}=\gamma_1$, $N_1=N_2=10^{-5}$. The solid curve is for $\theta=0°$ and the dashed curve for $\theta=90°$.

which clearly has only interference in spontaneous emission. To simplify the interference term we have taken $\omega_{13}/\omega_{23}\approx 1$.

In both the above cases either spontaneous or stimulated emission has interference. Thus, as seen in Sec. III, steady state coherence will be present. If we consider a single, unpolarized, broadband pumping field and nonorthogonal dipole matrix elements, then that will correspond to the situation $a=b=1$. The observational effect will be a dark line in the emission spectrum as seen in the case of thermal equilibrium. In the case of an asymmetric treatment, the observational effects will vary due to the steady state coherence. The dark line arises only for the case of symmetric treatment of spontaneous vs stimulated emission (results not shown).

VI. CONCLUSIONS

In conclusion, we have shown the consistency of dynamical equations with thermodynamic equilibrium. The quantum interferences lead to additional terms in the master equation. However, the structure of these additional terms is such that in the steady state we recover the Boltzmann distribution for populations and no coherences. We further discuss how the interference terms in the master equation can be probed. In particular, the interference terms result in a dark line in the emission spectrum. Further, we have shown that an asymmetric treatment of spontaneous vs stimulated emission can lead to results at variance with thermodynamic equilibrium. We also show how a broadband pumping gives additional freedom and how a variety of other steady states can be produced.

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APPENDIX: MULTILEVEL ATOM IN A THERMAL BATH

In this Appendix we prove a general result for the equilibrium state of a multilevel atom interacting with a thermal bath. The Hamiltonian for a multilevel atom in a thermal bath can be written as

$$H=\sum_{\mu} E_{\mu}A_{\mu\mu}+\sum_{ks}\hbar\omega_{ks}a_{ks}^{\dagger}a_{ks}+\sum_{\mu\neq\nu}V_{\mu\nu}A_{\mu\nu}, \tag{A1}$$

where

$$V_{\mu\nu}(t)=-i\sum_{ks}\left(\frac{2\pi ck}{L^3\hbar}\right)^{1/2}\vec{d}_{\mu\nu}\cdot(\hat{\epsilon}_{ks}a_{ks}e^{-i\omega_{ks}t} -\hat{\epsilon}_{ks}^{*}a_{ks}^{\dagger}e^{i\omega_{ks}t}). \tag{A2}$$

The generalized reduced master equation for this Hamiltonian in the Born-Markoff approximation is given by [20]

$$\frac{\partial\rho}{\partial t}=-i\left[\sum_{\mu}E_{\mu}A_{\mu\mu},\rho\right]+\sum_{\mu\nu\kappa\lambda}(A_{\kappa\nu}\rho_{\lambda\mu}-A_{\mu\lambda}\rho\delta_{\nu\kappa})\Gamma^{+}_{\mu\nu\kappa\lambda} +(A_{\mu\lambda}\rho_{\nu\kappa}-\rho A_{\kappa\nu}\delta_{\lambda\mu})\Gamma^{-}_{\kappa\lambda\mu\nu}, \tag{A3}$$

where

$$\Gamma^{+}_{\mu\nu\kappa\lambda}=\int_0^{\infty}\langle V_{\mu\nu}(t)V_{\kappa\lambda}(0)\rangle\exp(-i\omega_{\kappa\lambda}t)dt,$$
$$\Gamma^{-}_{\kappa\lambda\mu\nu}=\int_0^{\infty}\langle V_{\kappa\lambda}(0)V_{\mu\nu}(t)\rangle\exp(-i\omega_{\kappa\lambda}t)dt, \tag{A4}$$

$\langle V_{\mu\nu}(t)V_{\kappa\lambda}(0)\rangle=\mathrm{Tr}_R\{\rho_R(0)V_{\mu\nu}(t)V_{\kappa\lambda}(0)\}$ is the reservoir correlation function, $\hbar\omega_{\mu\nu}=(E_{\mu}-E_{\nu})$, and $\delta_{\mu\nu}$ is the Kronecker delta function. Here the energy spacings are assumed to be nondegenerate. In dealing with degenerate levels one needs to be careful about states decoupled from the reservoir as discussed at the end of Sec. III. The reservoir initially has a thermal distribution of photons given by

$$\rho_R(0)=\frac{\exp\left(-\beta\hbar\sum_{ks}\omega_{ks}a_{ks}^{\dagger}a_{ks}\right)}{\mathrm{Tr}_R\left\{\exp\left(-\beta\hbar\sum_{ks}\omega_{ks}a_{ks}^{\dagger}a_{ks}\right)\right\}}. \tag{A5}$$

It should be noted here that the above master equation (A3) is a generalized form which includes the nonsecular terms as well as the terms usually dropped under the rotating wave approximation. From Eqs. (A4) and (A5) we find that

$$\Gamma^{+}_{\mu\nu\kappa\lambda}=\begin{cases}\dfrac{2(\vec{d}_{\mu\nu}\cdot\vec{d}_{\kappa\lambda})\omega_{\kappa\lambda}^3}{3\hbar c^3}N(\omega_{\kappa\lambda}), & \omega_{\kappa\lambda}>0\\ \dfrac{2(\vec{d}_{\mu\nu}\cdot\vec{d}_{\kappa\lambda})\omega_{\lambda\kappa}^3}{3\hbar c^3}[1+N(\omega_{\lambda\kappa})], & \omega_{\kappa\lambda}<0,\end{cases} \tag{A6}$$

$$\Gamma^{-}_{\mu\nu\kappa\lambda}=\begin{cases}\dfrac{2(\vec{d}_{\mu\nu}\cdot\vec{d}_{\kappa\lambda})\omega^{3}_{\kappa\lambda}}{3\hbar c^{3}}[1+N(\omega_{\kappa\lambda})], & \omega_{\kappa\lambda}>0\\ \dfrac{2(\vec{d}_{\mu\nu}\cdot\vec{d}_{\kappa\lambda})\omega^{3}_{\lambda\kappa}}{3\hbar c^{3}}N(\omega_{\lambda\kappa}), & \omega_{\kappa\lambda}<0.\end{cases} \tag{A7}$$

Let us assume that a solution of the form $\rho=\exp(-\beta\Sigma_{\mu}E_{\mu}A_{\mu\mu})$ exists for Eq. (A3). Substituting this solution in Eq. (A3) we find that

$$\sum_{\mu\nu\kappa}A_{\mu\nu}\exp(-\beta E_{\kappa})[\Gamma^{+}_{\kappa\nu\mu\kappa}+\Gamma^{-}_{\kappa\nu\mu\kappa}-\Gamma^{+}_{\mu\kappa\kappa\nu}\exp(-\beta\hbar\omega_{\nu\kappa})-\Gamma^{-}_{\mu\kappa\kappa\nu}\exp(-\beta\hbar\omega_{\mu\kappa})]=0. \tag{A8}$$

From Eqs. (A6) and (A7) it can be shown that

$$\Gamma^{+}_{\kappa\nu\mu\kappa}=\Gamma^{-}_{\mu\kappa\kappa\nu}\exp(-\beta\hbar\omega_{\mu\kappa}), \tag{A9}$$

$$\Gamma^{-}_{\kappa\nu\mu\kappa}=\Gamma^{+}_{\mu\kappa\kappa\nu}\exp(-\beta\hbar\omega_{\nu\kappa}). \tag{A10}$$

Using Eqs. (A9) and (A10) we find that Eq. (A8) is satisfied. This shows that the steady state solution is in fact Boltzmann distribution for populations, and as long as there are no atomic states decoupled from the reservoir the steady state solution is unique.

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