Magnetically Driven Maser Effect in the Resonant Dynamics of V_{15} Molecular Nanomagnets

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Resonant dynamics of magnetic molecules with spin 1/2 ground state, such as V_{15}, is theoretically studied. In our model calculation, crystals of this molecular nanomagnet are probed by time-dependent magnetic fields, which continuously invert populations of spin states. If the sample is placed in a resonant cavity, relaxation of excited states, via spin-photon interaction, allows for stimulated emission of radiation in the microwave range at resonance.

Keywords: Molecular magnets; Spin dynamics; Maser; Nanomagnets

I. INTRODUCTION

Recent interest on molecular nanomagnets has grown significantly due to the spectacular magnetic effects they exhibit, namely the pronounced magnetic hysteresis and the quantization of the magnetic moment[1]. Potential applications of such magnets for current and future technologies include information storage, construction of nanomagnetic Maser-like devices, and quantum computation. The name Single-Molecule Magnets (SMM) has been coined to mean that individual molecules act as magnets. They can be prepared in long-lived excited quantum states by simply applying a magnetic field[2], and exhibit a stepwise magnetic hysteresis in a time-dependent magnetic field. Quantum relaxation of spin states at low temperatures is very sluggish, and has been intensively studied within the framework of the Landau-Zener-Stueckelberg(LZS) effect[3–5]. Large spin high-anisotropic SMM are on the verge between classical and quantum objects. For large spin, the dipolar interaction may remain as the relevant coupling between molecules, its relative effect being proportional to the square of the spin value[6]. On the other hand, low spin and weakly anisotropic SMM are strong candidates to perform quantum computation, since they display quantum coherence and show a slow relaxation of the magnetization, in spite of the absence of any anisotropy energy barrier. A protoype of such a system is the molecular complex V_{15}[7], whose ground state has $S=1/2$, with a weak anisotropy and no dipolar interactions between molecules. The low value of the spin is due to antiferromagnetic coupling between $V^{4+}(S=1/2)$ ions within the molecular complex. The molecule structure is very peculiar, with two almost planar hexagons sandwiching a central triangle. Spins of the hexagons form closed antiferromagnetic rings, since frustration effects decouple the triangle from the hexagons. As a net result, one describes its magnetic properties using a simple antiferromagnetic (AFM) Heisenberg model on a triangle:

$$\mathcal{H} = J_0\left(\mathbf{S_1}\cdot\mathbf{S_2}+\mathbf{S_2}\cdot\mathbf{S_3}+\mathbf{S_3}\cdot\mathbf{S_1}\right), \tag{1}$$

where $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$ are the spin operators ($S=1/2$) for the three sites, respectively, and $J_0>0$ is the AFM coupling. The ground state of this system consists of two degenerate Kramers doublets ($S=1/2$), with a $S=3/2$ excited state separated from the ground by an energy of the order of $3.8K$. The ground state has been probed by recent resonant photon absorption experiments, which support the single-molecule interpretation picture[8]. Inelastic neutron scattering experiments suggest that the ground state degeneracy is partly lifted by deviations from trigonal symmetry and the presence of the Dzyaloshinskii-Moriya interaction, but the effect is very small compared to the energy that separates the spin 1/2 ground from the excited spin 3/2 state[9]. At any rate, the Kramers degeneracy can not be lifted, and the ground state is at least double degenerate. Throughout this paper, we will consider only two states ($m=-1/2$ and $m=+1/2$) as relevant to the problem, and we will ignore the splitting between the two Kramers doublets. Our aim in this paper is to study the effect of stimulated radiation from molecular nanomagnetic crystals, considering a fully quantum mechanical model, in which the electromagnetic radiation enters as a quantized field. In this context, a striking effect has been predicted[10], where molecular nanomagnetic crystals exhibit a giant magnetic relaxation due to Dicke superradiance of electromagnetic waves [11]. In recent electron spin resonance (EPR) experiments, it has been observed a pronounceable resonant absorption of electromagnetic radiation by molecular nanomagnets[12–16]. In turn, they become a powerful source of coherent electromagnetic radiation when the wavelength of the emitted photons exceeds the linear size of crystals. When this condition is achieved, the molecules can coherently interact with the radiation emmitted, and the phase of the emitted photons may be considered the same throughout the sample[10]. Inside a resonant cavity, molecular magnets exhibit a strong dependence of the magnetization on the geometry of the cavity and this effect was observed experimentally, providing strong evidence for the coherent microwave radiation given off by the crystals. These observations open the possibility of building nanomagnetic microwave lasers pumped by magnetic fields[17].

In this paper, we adopt a model, whose essential ingredients include:

i) coupling of individual spin 1/2 molecules with a time-varying magnetic field $B_z(t)$ along the quantization axis. This way, the low and high energy states will be continuously changing with time, creating the effect of spin-population inversion. Note that this is different from most models proposed in the literature, where the magnetic field B_z is constant, and a time-dependent field is applied in the transverse direction;

ii) a quantized electromagnetic field inside a resonant cavity, which allows the relaxation of excited states by means of coherent photon emission, enhancing the radiation field.

Finally, we will analize the semiclassical limit, in which the photon-field can be treated as a classical electromagnetic field. The content of the paper can be described as follows: in the next Section, we formulate the theoretical basis for analyzing spin dynamics, discussing the Hamiltonian. In Section III, we analyze the dynamics of a pure quantum mechanical state initially prepared in one of the double degenerate ground states of the system. We compute the correlation amplitude between the initial and the evolved state. Analytical approximated expressions are obtained to be compared with numerical results. In Section IV, we consider the photon field as a classical variable and obtain, in close analytical way, the conditions for a maser-like effect. Finally, in the last Section a few conclusions and remarks are added.

II. HAMILTONIAN AND QUANTUM DYNAMICS

We start considering the two lowest-level states ($S = 1/2$, with $m = +1/2$ and $m = -1/2$) of a molecule and a second quantized term in photon variables describing the radiation field in the cavity:

$$\mathcal{H}_0 = -g\mu_B S B_0(t)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \hbar\omega a^\dagger a \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad (2)$$

where the Pauli matrix

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

yields the splitting of the levels in the presence of a time-dependent magnetic field $B_0(t)$ applied along the quantization axis. The operator $a^\dagger (a)$ is the photon creation (annihilation) operator. Inside a resonant cavity, only photons with a preselected frequency ω can be emitted or absorbed. The basis of $\mathcal{H}_0$ is given through the kets $\{|S,n>\}$ and $\{|-S,n>\}$, being n the number of photons in a given state. We will consider that a general state can be written as follows:

$$|\Psi >= \{A_S|S> + A_{-S}|-S>\} \otimes \sum_{n=0}^{\infty} \alpha_n |n>$$

The interaction between the molecular spin and the dipolar component of the electromagnetic radiation inside the cavity is considered as a perturbation:

$$\mathcal{H}_I = -\hbar\Gamma \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} (a^\dagger + a) , \qquad (3)$$

where the Pauli matrix

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

flips the molecule from one level to the other (with the emission or absorption of a photon). One can see that our model consists of a two level system coupled to a quantized harmonic oscillator. Despite the simplicity of the above mentioned model, no exact analytic solution is yet known[18]. Now, we consider the quantum dynamics in the interaction picture, taking into account that the non-perturbed (diagonal) hamiltonian $\mathcal{H}_0$ is time dependent. In this case, operators evolve according to the equation:

$$i\hbar \frac{\partial O}{\partial t} = [O, \mathcal{H}_0]$$

and for the interaction Hamiltonian we get

$$\mathcal{H}_I(t) = e^{iW(t)} \mathcal{H}_I e^{-iW(t)} , \qquad (4)$$

being

$$W(t) = \frac{1}{\hbar} \int_0^t \mathcal{H}_0(t') dt' \qquad (5)$$

The temporal evolution of an initial state ket $|\Psi_0>$ will be given by the unitary evolution operator U_I in the interaction picture. The latter can be written in the form of a Dyson series:

$$U_I(t,0) = 1 - \frac{i}{\hbar} \int_0^t dt_1 e^{iW(t_1)} \mathcal{H}_I e^{-iW(t_1)} + $$
$$+ \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 e^{iW(t_1)} \mathcal{H}_I e^{-iW(t_1)} \int_0^{t_1} dt_2 e^{iW(t_2)} \mathcal{H}_I e^{-iW(t_2)} + \dots , \qquad (6)$$

with $|\Psi(t)> = U_I(t,0)|\Psi_0>$. We can express the interaction hamiltonian $\mathcal{H}_I$ in the form below:

$$e^{iW(t)} \mathcal{H}_I e^{-iW(t)} = -\hbar\Gamma \begin{pmatrix} 0 & H_{12} \\ H_{21} & 0 \end{pmatrix}, \qquad (7)$$

being

$$\begin{aligned} H_{12} &= a^{\dagger}\exp\left[i\left(\omega t-\frac{2g\mu_B S}{\hbar}\int_0^t B_0(t')dt'\right)\right]+ \\ &\quad +a\exp\left[-i\left(\omega t+\frac{2g\mu_B S}{\hbar}\int_0^t B_0(t')dt'\right)\right] \qquad (8) \\ H_{21} &= H_{12}^{\dagger}=a^{\dagger}\exp\left[i\left(\omega t+\frac{2g\mu_B S}{\hbar}\int_0^t B_0(t')dt'\right)\right]+ \\ &\quad +a\exp\left[-i\left(\omega t-\frac{2g\mu_B S}{\hbar}\int_0^t B_0(t')dt'\right)\right] \qquad (9) \end{aligned}$$

One must remember that H_{12} and H_{21} are infinite-dimensional in the Fock space of photons. We write U_I in the following form

$$\begin{aligned} U_I &= 1+i\Gamma\int_0^t dt_1\begin{pmatrix} 0 & H_{12}(t_1) \\ H_{21}(t_1) & 0 \end{pmatrix}- \\ &\quad -\Gamma^2\int_0^t dt_1\int_0^{t_1} dt_2\begin{pmatrix} H_{12}(t_1)H_{21}(t_2) & 0 \\ 0 & H_{21}(t_1)H_{12}(t_2)\ f \end{pmatrix}+\ldots \qquad (10) \end{aligned}$$

The above expressions admit any time-varying magnetic field $B_0(t)$. For sake of convenience, we will restrict our attention to the sinusoidal dependence:

$$B_0(t)=B_0\cos(\Omega t), \qquad (11)$$

and in this case (8) and (9) reduce to

$$\begin{aligned} H_{12}(t) &= a^{\dagger}\exp\left[i\left(\omega t-r\sin(\Omega t)\right)\right]+a\exp\left[-i\left(\omega t+r\sin(\Omega t)\right)\right], \qquad (12) \\ H_{21}(t) &= a^{\dagger}\exp\left[i\left(\omega t+r\sin(\Omega t)\right)\right]+a\exp\left[-i\left(\omega t-r\sin(\Omega t)\right)\right], \qquad (13) \end{aligned}$$

where we have defined

$$r=\frac{2g\mu_B SB_0}{\hbar\Omega}. \qquad (14)$$

The frequency Γ in $\mathcal{H}_I$ represents the coupling with the dipolar field, and is small when the wavelength of the radiation field is far longer than the molecular dimension. In this case, first order perturbation theory applies, leading to:

$$U_I=1+i\Gamma\mathcal{M}_1+O(\Gamma^2) \qquad (15)$$

and

$$\mathcal{M}_1=\begin{pmatrix} 0 & a^{\dagger}F_1+aF_2 \\ a^{\dagger}F_2^*+aF_1^* & 0 \end{pmatrix}. \qquad (16)$$

The dynamics of the system will be governed by the functions $F_1(t)$ and $F_2(t)$:

$$\begin{aligned} F_1(t) &= \int_0^t dt_1\exp[i[\omega t_1-r\sin(\Omega t_1)]]=\frac{J_0(r)}{i\omega}(e^{i\omega t}-1)+ \\ &\quad +2\sum_{m=0}^{\infty}\left[\frac{J_{2m+2}(r)}{\omega^2-(2m+2)^2\Omega^2}\Lambda_{1,m}(t)-i\frac{J_{2m+1}(r)}{\omega^2-(2m+1)^2\Omega^2}\Lambda_{2,m}(t)\right], \qquad (17) \\ F_2(t) &= \int_0^t dt_1\exp[-i[\omega t_1+r\sin(\Omega t_1)]]=\frac{J_0(r)}{i\omega}(1-e^{-i\omega t})+ \\ &\quad +2\sum_{m=0}^{\infty}\left[\frac{J_{2m+2}(r)}{\omega^2-(2m+2)^2\Omega^2}\Lambda_{1,m}^*(t)-i\frac{J_{2m+1}(r)}{\omega^2-(2m+1)^2\Omega^2}\Lambda_{2,m}^*(t)\right], \qquad (18) \end{aligned}$$

being $J_{2m+1}(r)$ and $J_{2m+2}(r)$ the Bessel functions of first kind, and

$$\begin{aligned} \Lambda_{1,m}(t) &= i\omega-i\omega e^{i\omega t}\cos[(2m+2)\Omega t]-(2m+2)\Omega e^{i\omega t}\sin[(2m+2)\Omega t] \qquad (19) \\ \Lambda_{2,m}(t) &= -i\omega e^{i\omega t}\sin[(2m+1)\Omega t]+(2m+1)\Omega e^{i\omega t}\cos[(2m+1)\Omega t]-(2m+1)\Omega. \qquad (20) \end{aligned}$$

From the above formulae, a resonant behavior occurs when the photon frequency ω is an integer multiple of Ω, say $\omega = m\Omega$, and the dominant behavior of F_1 and F_2 near that condition is given by:

$$F_1 \approx \frac{J_m(r)[(-1)^m i(1-e^{2i\omega t})+2t\omega]}{2\omega} \tag{21}$$

$$F_2 \approx (-1)^m F_1^* = (-1)^m \frac{J_m(r)[(-1)^{m+1} i(1-e^{-2i\omega t})+2t\omega]}{2\omega} \tag{22}$$

In the next Section we will analyze the dynamics of a pure quantum mechanical state initially prepared as an eigenstate of $\mathcal{H}_0$.

III. DYNAMICS OF QUANTUM STATES

To fix ideas, consider a quantum state prepared in the magnetic state $|S=+1/2>$ of the molecule, in the form:

$$|\Psi_0>=|S>\sum_{n=0}^{\infty}\alpha_n|n> \tag{23}$$

where the mean number of photons at $t=0$ is given by

$$n_0 = <a^\dagger a>_0 = \sum_{n=0}^{\infty} n|\alpha_n|^2 .$$

To first order perturbation theory, the evolved state $|\Psi(t)>= U_I|\Psi_0>$ reads

$$|\Psi(t)> \approx \frac{1}{\sqrt{1+\Gamma^2[(n_0+1)|F_2|^2+n_0|F_1|^2}} \times \\ \times \left[|\Psi_0> + i\Gamma|-S>\sum_{n=0}^{\infty}\alpha_n\left(F_2^*\sqrt{n+1}|n+1> + F_1^*\sqrt{n}|n-1>\right)\right]. \tag{24}$$

Observe that we have renormalized the evolved state. The correlation probability function defined as $C(t) = |<\Psi_0|\Psi(t)>|^2$, which is simply the probability of finding the system in the initial state at later times, yields

$$C(t) = \frac{1}{1+\Gamma^2[(n_0+1)|F_2|^2+n_0|F_1|^2]} , \tag{25}$$

and the above expression can be approximated at the resonant condition $\omega = m\Omega$ by the behavior of F_1 and F_2 given in (21) and (22):

$$C(t) \approx \frac{1}{1+\Gamma^2|F_1|^2(2n_0+1)}, \tag{26}$$

with

$$|F_1|^2 = \frac{|J_m(r)|^2}{4\omega^2}\left(4\sin^2\omega t + 4t\omega\sin 2\omega t + 4\omega^2 t^2\right).$$

For long times ($t\omega \gg 1$), the leading behavior is quadratic in time

$$|F_1|^2 \approx |J_m(r)|^2 t^2 ,$$

and we can approximate the above expression as follows:

$$C(t) \approx \frac{1}{1+t^2/\tau^2} , \tag{27}$$

with the correlation time τ defined as:

$$\frac{1}{\tau} = \Gamma|J_m(r)|\sqrt{2n_0+1}. \tag{28}$$

The value $1/\tau$ can be interpreted as the rate of emission of photons, since the nanomagnet will relax to lower energy states by emitting photons. For large values of the constant r, maxima of the transition rate will be given by $r = 2gS\mu_B B_0/(\hbar\omega/m) \sim \zeta\pi$, with $\zeta \gg 1$ a constant depending on the order of the Bessel function, yielding

$$\left(\frac{1}{\tau}\right)_{\max} \approx \Gamma\sqrt{\frac{\hbar(\omega/m))}{\pi g S\mu_B B_0}}\sqrt{2n_0+1}.$$

Next, we show some examples. To illustrate the evolution of a quantum state, we consider the initial mean number of photons $n_0 = 0$, *i.e.* the vacuum for the cavity field, and the molecular spin in the $S = 1/2$ state (in this case the initial state is $|\Psi_0>=|S,0>$). The resonant cavity is adjusted to the frequency $f = \omega/2\pi = 10$ GHz and the spin-photon interaction constant is taken as $\Gamma = 2$ GHz. In Fig. 1 to 3, we show the correlation probability $C(t)$ as a function of time, for given values of r and $m = \omega/\Omega$. At a given ratio $m = \omega/\Omega$, the parameter r was set to give the maximum value of the Bessel function $J_m(r)$. The parameters for the first two figures satisfy the resonant condition (m an integer). One can see that the behavior for m even or odd is qualitatively the same. Except for the stepwise character of the correlation function, the overall behavior of $C(t)$ can be estimated by the expression (27), with the relaxation time given by (28). Note the irreversible character of $C(t)$ at the resonance, due to the relaxation of the molecule by successive photon emissions, which occurs in time at integer multiples of the period $T = 2\pi/\Omega$.

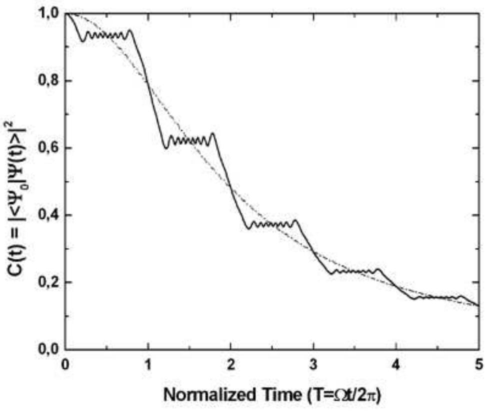

FIG. 1: Correlation function $C(t)$ as a function of time, considering $\Gamma = 2\times10^9$ s^{-1}, $\omega = 2\pi\times10^{10}$ rad/s, $\Omega = \omega/m$, $m = 8$ and $r = 9,65$. The dotted line corresponds to the approximate behavior given by eq. (27).

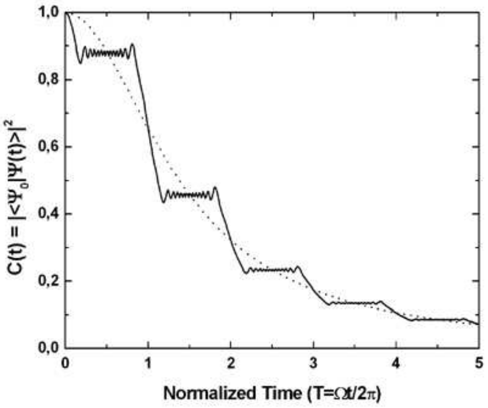

FIG. 2: Correlation function $C(t)$ with parameters Γ and ω kept the same as for the previous figure, $m = 11$ and $r = 11,94$. The dotted line corresponds to the approximate behavior given by eq. (27).

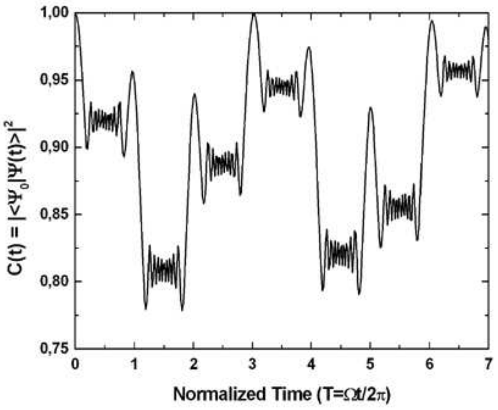

FIG. 3: Correlation function $C(t)$ for a non-integer ratio ω/Ω. In this case we have chosen $m = 9,31$ and $r = 11,45$.

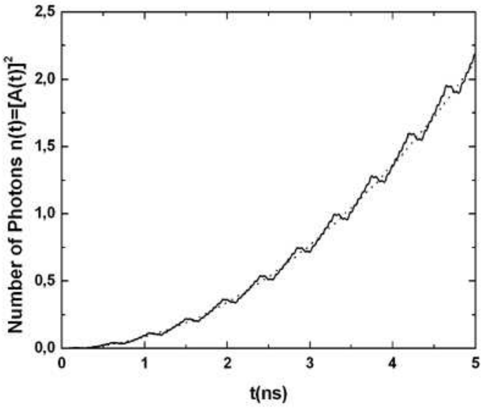

FIG. 4: Number of photons for the field $\langle n\rangle = |A(t)|^2$ in the semiclassical approximation using $f = \omega/2\pi = 10$ GHz, $\Gamma = 1$ GHz, $M_0 = 0$, $N_0 = 0.5$, $n_0 = 0$, $m = 9$ and $r = 10$. The dotted line corresponds to the approximated solution (40).

A quite different situation occurs for a non-integer value of the ratio ω/Ω, as shown in Fig. 3 for $m = 9,31$. There are revivals of the initial state at latter times, in the form of an absorption-emission cycle not completely periodic.

The above results were obtained within first order perturbation theory. Consequently, the long-time behavior should include corrections due to multiple photon processes. However, we believe that the essential physics is contained in the results discussed above. To support this view, in the next section we analyze the radiation field using the semiclassical approximation. We predict a masser effect at resonances.

IV. SEMICLASSICAL THEORY

The semiclassical theory is based on two fundamental assumptions: i) the cavity radiation field is described by a coherent state, which is the most nearly classical state (it minimizes the uncertainty relations); ii) the total density matrix is written as a product, whose factors are related to spin and photon degrees of freedom. In other words, we assume that spin variables are uncorrelated with those of the field[19]. For

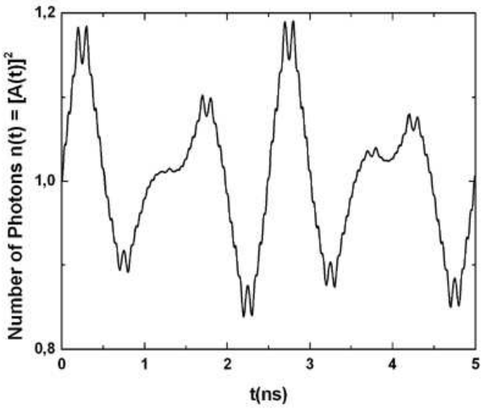

FIG. 5: Number of photons for the field $\langle n\rangle = |A(t)|^2$ in the semiclassical approximation using $f = \omega/2\pi = 10$ GHz, $\Gamma = 1$ GHz, $M_0 = 0$, $N_0 = 0.5$, $n_0 = 1$, $m = 10$ and $r = 12$.

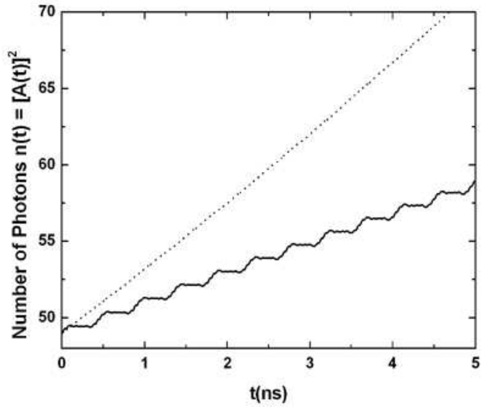

FIG. 6: Number of photons for the field $\langle n\rangle = |A(t)|^2$ in the semiclassical approximation with f, Γ, $M_0 = 0$ and $N_0 = 0.5$ kept the same as the previous case, $n_0 = 49$, $m = 9$ and $r = 10$. The dotted line corresponds to the approximated solution (40).

a coherent state $|z\rangle$, we have the results

$$\begin{aligned} a|z\rangle &= z|z\rangle, & (29)\\ \langle z|a^\dagger &= \langle z|z^*, & (30)\\ \langle n\rangle &= |z|^2. & (31) \end{aligned}$$

So, the semiclassical approximation can be thought to be obtained by replacing the photon operators by complex numbers. Chosing the amplitude of the coherent state as real, we get $a^\dagger, a \rightarrow \sqrt{\langle n\rangle}$. Then the equation of motion for the mean number of photons $\langle n\rangle$ will be given by:

$$\frac{dA}{dt} = -\Gamma\sin(\omega t)[\rho_{12}e^{ir\sin(\Omega t)} + \rho_{21}e^{-ir\sin(\Omega t)}] \qquad (32)$$

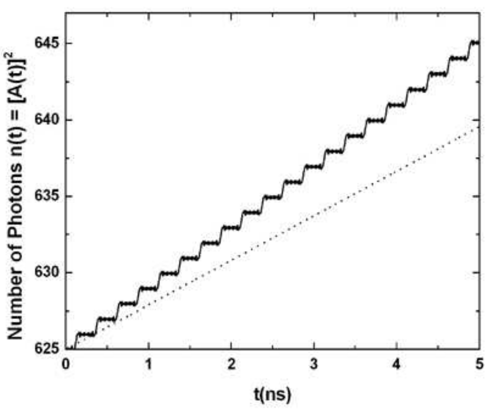

FIG. 7: Number of photons for the field $\langle n\rangle = |A(t)|^2$ in the semiclassical approximation obtained from equations (32)-(35) using $M_0 = 0$, $\rho_{12}(0) = \rho_{21}^*(0) = iN_0 = 0.5i$, $n_0 = 625$, $m = 5$ and $r = 45$. The dotted line is the approximated number of photons given by eq.(40). The dotted line corresponds to the approximated solution (40).

with $A = \sqrt{\langle n\rangle}$. The density matrix ρ of the spin system satisfies the following set of coupled equations:

$$\begin{aligned} \frac{\partial M}{\partial t} &= 4i\Gamma[\rho_{21}e^{-ir\sin(\Omega t)} - \rho_{12}e^{ir\sin(\Omega t)}]A\cos(\omega t) & (33)\\ \frac{\partial \rho_{12}}{\partial t} &= -2i\Gamma e^{-ir\sin(\Omega t)}MA\cos(\omega t) & (34)\\ \frac{\partial \rho_{21}}{\partial t} &= 2i\Gamma e^{ir\sin(\Omega t)}MA\cos(\omega t), & (35) \end{aligned}$$

where $M = \rho_{11} - \rho_{22}$. In general the solution must be accomplished by numerical methods. A simple solution is obtained if one assumes $\rho_{12} = \rho_{21}^* = iN$, being $\rho_{12} - \rho_{21} = 2iN$, *i.e.* the off-diagonal elements depends on a single real parameter. It can be shown that the other possibilty, $\rho_{12} = \rho_{21} = R$ does not lead to a maser effect. For the former case we have:

$$\begin{aligned} \frac{\partial M}{\partial t} &= 8\Gamma NA\cos(r\sin(\Omega t))\cos(\omega t), & (36)\\ \frac{\partial N}{\partial t} &= -2\Gamma MA\cos(r\sin(\Omega t))\cos(\omega t), & (37)\\ \frac{dA}{dt} &= 2\Gamma N\sin(r\sin(\Omega t))\sin(\omega t). & (38) \end{aligned}$$

An approximate solution near the initial value $A_0 \approx 0$ for the photon field A is easily obtained, yielding:

$$A(t) = A_0 + \Gamma N_0 \mathrm{Re}(F_1 - F_2) \qquad (39)$$

In the case of $\omega = (2m+1)\Omega$ the above solution for A grows linearly with time:

$$A(t) \approx A_0 + 2\Gamma N_0 J_{2m+1}(r)\left(t - \frac{\sin(2\omega t)}{2\omega}\right) \qquad (40)$$

and consequently, the number of photons increases quadratically with time. In contrast, for $\omega = (2m+2)\Omega$ the approximate solution is nearly constant, with $A(t) \approx A_0$, displaying ripples around this value. This even-odd symmetry breaking at resonance, is at variance with the pure quantum case treated in the previous section, where both resonance conditions presented similar behaviors, *i.e.* an increase of the photon number due to relaxation of the molecular states, no matter if m was even or odd. In any case, for the semiclassical approximation, a maser effect is predicted for $\omega = (2m+1)\Omega$. To illustrate this phenomenon, we show in Figs. 4 to 7, the photon number as a function of time, for some temperatures. In Fig. 4 and 5, we take the limit $k_BT \to 0$, and the initial photon number $n_0 \to 0 (A_0 \to 0)$. Other parameter values are $M_0 = 0$ and $N_0 = 0.5$. In Fig. 4, we have chosen $n_0 = 0$, $m = 9$ and $r = 10$, while for Fig. 5, $n_0 = 1$, $m = 10$ and $r = 12$ (the corresponding value of r is always chosen to maximize the Bessel function). From Fig. 4, it is clear that the overall behavior of the photon number for m odd is closely related to the solution given by expression (40), and shown by the dashed line, corresponding to a quadratic increase of the number of photons with time. In contrast, when m is even, there is an oscillatory behavior, at least for short times, which reminds the quantum revivals. Figures 6 and 7 refer to examples at finite temperatures for m odd. For Fig. 6, $T = 24$ K, corresponding to the initial value $n_0 = k_BT/(\hbar\omega) = 49$ for the number of photons, while Fig. 7 is at room temperature ($T = 300$K), corresponding to $n_0 = 625$ photons. Fig. 7 was obtained solving numerically the full set of equations (32)-(35) due to the fact that for high number of photons the system clearly displays nonlinearities and the real part of ρ_{12} grows significantly with time. We have taken the initial values $\rho_{12}(0) = \rho_{21}^*(0) = 0.5i = iN_0$. It is clear that the photon number will increase inside the cavity. In practice, it will increase until a saturation limit. The divergent behavior here obtained is due to the fact that losses are not taken into account. Such losses are provided by photons leaving the cavity and by excitation of other energy states. In fact, the real system which we are concerned here, is not as simple as a two-level object. In addition, the cavity field should include contributions from other photon modes, which we neglected from the beginning.

V. CONCLUSIONS

We have developed the quantum dynamics of molecular nanomagnets, taking into account the quantized photon field of the cavity. In first approximation, the magnetic molecules were treated as two-level systems. The temporal evolution of quantum states were studied in details in this paper, considering a time-varying magnetic field $B_z(t) = B_0\cos(\Omega t)$, applied along the quantization direction. The above field produces the necessary population inversion in a periodic way.

The spin system couples with the dipolar component of the cavity field, allowing transitions between both molecular states with photon emission and absorption. The emission of photons is enhanced at the resonant condition, when the ratio between photon frequency ω and the applied field frequency Ω is an integer number $m = \omega/\Omega$. At resonance, the energy is pumped from the applied magnetic field to the cavity radiation field, inducing a relaxation process depicted by Fig. 1 and 2. This striking phenomenon was illustrated in the previous section, via the semiclassical theory. In turn, the case of non-integer m produces a revival of the initial state, which means that emission and absorption of photons occur in almost periodic sequences, very similar to Rabi periods.

Qualitative insights can be obtained via the semiclassical approximation, which is more suitable for practical purposes at room temperatures. Within this theory, the macroscopic state of the cavity field is described by the coherent states introduced by Glauber [20]. In this case, a maser effect is obtained at resonance, only when m is an odd number. When the temperature is increased, the initial photon number is also increased, and the dynamics is complicated by non-linear effects.

While the description of individual molecular complexes must be intrinsically quantum mechanical, large assemblies of molecules (as for instance, in a crystal) can be treated by semiclassical techniques with good accuracy. The theory developed in this paper applies to the case of V_{15} molecular complexes. Typical values of parameters are found in Ref. [8]. The spin 1/2 ground state shows resonant photon absorption in the 1-20 GHz range, with applied magnetic fields of the order of 0.1-1 T. Wavelength of the radiation, for the above frequency values, ranges from 2 to 20 cm (microwave range). If we adopt the above values for our model, we expect a cooperative behavior, encompassing the whole system, of molecules interacting coherently with the radiation field.

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