Superradiance from crystals of molecular nanomagnets

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We show that crystals of molecular nanomagnets can exhibit giant magnetic relaxation due to the Dicke superradiance of electromagnetic waves. Rigorous treatment of the superradiance induced by a field pulse is presented.

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High-spin molecular nanomagnets, such as spin-10 Mn\(_{12}\) and Fe\(_{8}\), represent the boundary between classical and quantum physics. On one hand, they exhibit pronounced magnetic hysteresis, as classical magnets do. On the other hand, the very same magnetization curve reveals quantum nature of spin [1]. These unique properties of molecular nanomagnets are consequence of long-living metastable spin states [2] due to the large value of spin and high energy barriers. The lifetime of these states is believed to be dominated by spin-phonon processes [3, 4] and by quantum spin tunneling [5, 6, 7, 8]. The latter, for a field-sweep experiment, has been successfully described in terms of single-molecule Landau-Zener (LZ) transitions [9, 10, 11, 12, 13].

Recent ESR experiments [13, 14, 15, 16, 17] have demonstrated noticeable resonant absorption of electromagnetic radiation by molecular magnets. In this Letter we show that crystals of magnetic molecules can also be a powerful source of coherent electromagnetic radiation. At low fields, the magnetic relaxation of molecular nanomagnets may be affected by the distribution of energy levels due to dipolar fields [22], nuclear spins [22, 23], and crystal defects [13]. Here we will study the case when the resonant tunneling of the spin of individual molecules is dominated by the large external magnetic field (or by a large transverse anisotropy). We will be interested in relaxation between the tunnel-splitted ground states of the system in the wells are described by metastable spin states [2] due to the large value of spin [1]. These unique properties of molecular nanomagnets are consequence of long-living metastable spin states [2] due to the large value of spin

\[ \varepsilon_\pm = \frac{1}{2} \left( \varepsilon_2 + \varepsilon_1 \pm \sqrt{W^2 + \Delta^2} \right), \]

(1)

where \( W \equiv \varepsilon_1 - \varepsilon_2 \), and the eigenstates are given by

\[ \psi_\pm = \frac{1}{\sqrt{2}} (\pm C_\pm \psi_1 + C_\mp \psi_2) \]

(2)

with \( C_\pm = \pm W/\sqrt{\Delta^2 + W^2} \) [13]. Here \( \psi_1 \) and \( \psi_2 \) are eigenstates in the left and right wells with tunneling neglected. If the transverse field \( H_x \) is small, the states \( \psi_1 \) and \( \psi_2 \) are just \( |S\rangle \) and \(-|S\rangle \). In the strong field the ground states of the system in the wells are described by the tilted spin and its projection \( \langle S_z \rangle_0 \). In this case

\[ W = 2\langle S_z \rangle_0 g\mu_B H_z, \]

(3)

For \( S \gg 1 \) the classical approximation for \( \langle S_z \rangle_0 \) works well. In particular, for Mn\(_{12}\) \((H = -DS_y^2 - g\mu_B H_x S_x)\)
Eq. (5) at \( W \) is the photon frequency. The matrix element squared is \( / \Delta \), refraction index of the crystal, and where \( \Delta \) gives \( \Gamma \) and \( \Delta \) are produced when we begin with all magnetic molecules in the left well in Fig. 1, that is, magnetized down, and then sweep the applied field across the resonance. The dynamics of the system is that of a large spin \( R \) coupled to photons, and it is convenient to label its states by the quantum number \( M \) which is the projection of \( R \) on \( H_{\text{eff}} \) of Eq. (9). The matrix elements of the Hamiltonian Eq. (8) for transitions between \( |R, M \rangle \) contain factors \( \sqrt{(R \pm M)(R \mp M + 1)} \) that are additional to those for a single molecule. The latter makes the spontaneous radiation power \( I \) to scale as \( (R + M)(R - M + 1) \). If \( |M| \ll R \) and \( R \sim N \), then \( I \propto N^2 \), which is \( N \) times the incoherent radiation from a system of \( N \) molecules. This is the superradiance discovered by Dicke [22].

At finite temperatures, the time evolution of a system of tunneling molecules in equilibrium with the radiation field is described by the density-matrix equation (DME) for a spin \( R \). For \( R \gg 1 \) and low temperatures, \( R g \mu_B H_{\text{eff}} / (k_B T) = R \omega / (k_B T) \gg 1 \) (but not necessarily \( \hbar \omega / (k_B T) \gg 1 \), see Ref. [27]), this DME goes over to the classical Landau-Lifshitz equation,

\[
\dot{n} = \gamma [n \times H_{\text{eff}}] - \alpha [n \times |n \times H_{\text{eff}}|], \quad n \equiv R / R, \quad (10)
\]

where \( \gamma = g \mu_B / \hbar \) is the gyromagnetic ratio, \( \alpha = R \Gamma_1 / \gamma H_{\text{eff}} \tanh \left( g \mu_B H_{\text{eff}} / 2 k_B T \right) \) (11) is dimensionless damping coefficient, \( \Gamma_1 \) is given by Eq. (6) and \( H_{\text{eff}} \) is defined by Eq. (9).

The first term in Eq. (10) gives dissipationless Landau-Zener transitions when the field is swept through the resonance such that \( W = W(t) \) satisfies \( W(\pm \infty) = \pm \infty \), and the initial condition is \( n(-\infty) = -e_\omega \). Indeed, the Schrödinger equation for a two-level system is equivalent to the equation for a precessing spin. The probability \( P(t) \) for a molecule to stay in the initial state is given by

\[
P(t) = [1 - n_z(t)]/2. \quad (12)
\]

For \( W(t) = vt \), one obtains the LZ result [4, 10]

\[
P(\infty) \equiv P = \exp[-\pi \Delta^2 / (2 \hbar v)]. \quad (13)
\]
The second term in Eq. (10) describes Dicke superradiance since \( \alpha \) contains the large factor \( R = N/2 \). Eqs. (11), (12), (13) and relation \( g \mu_B H_{\text{eff}} = \sqrt{\Delta^2 + W^2} \) yield

\[
\alpha = \frac{1}{6} N \langle S_z \rangle^2 g^2 \mu^3 \left( \frac{e^2}{\hbar c} \right) \left( \frac{\Delta}{m_e c^2} \right)^2 ,
\]

where \( e \) is electron charge, \( m_e \) is electron mass and \( c \) is the speed of light. Note that \( \alpha \) is independent of the energy bias \( W \). The corresponding longitudinal decay rate is

\[
\Gamma = 2 \alpha \gamma H_{\text{eff}} = 2 \alpha \omega = 2 R \Gamma_1^{(0)} = N \Gamma_1^{(0)},
\]

where \( \Gamma_1^{(0)} \) is given by Eq. (13) without the coth factor. Thus superradiance boosts the one-molecule relaxation rate by a macroscopically large factor \( N \).

Let us consider at first the solution of Eq. (10) for \( H_{\text{eff}} = \text{const.} \) in this case it is convenient to describe the motion of the Dicke pseudospin \( n \) in the coordinate system with the \( z' \) axis along \( H_{\text{eff}} \). The physically relevant \( z \) component of \( n \) is given by

\[
n_z = n_{z'} \cos \psi - n_{x'} \sin \psi, \quad \cos \psi = \frac{W}{\sqrt{\Delta^2 + W^2}},
\]

whereas the solution for \( n_{z'} \) and \( n_{x'} \) reads

\[
n_{z'}(t) = \frac{\sinh(\tau) + n_{z'}(0) \cosh(\tau)}{\cosh(\tau) + n_{z'}(0) \sinh(\tau)}, \quad \tau = \alpha \gamma H_{\text{eff}} t,
\]

\[
n_{x'}(t) = \sqrt{1 - n_{z'}^2(t)} \sin(\gamma H_{\text{eff}} t + \phi_0).
\]

The full relaxation from \( n_{z'} = -1 \) to \( n_{z'} = 1 \) is given by \( n_{z'}(t) = \tanh(\tau) \) which can be used to obtain the value of \( \alpha \) from an independent macroscopic argument. To this end, we set \( R = N/2 \) and equate the change of Zeeman energy \( N g \mu_B H_{\text{eff}} \) [see Eq. (1)] to the energy dissipated due to the magnetic-dipole radiation

\[
I = \int \frac{\Delta^2 + W^2}{\hbar v} \nu d
\]

where \( m_z = N \langle S_z \rangle \) \( g \mu_B \) \( n_z \). For \( \alpha \ll 1 \) one obtains

\[
\bar{n}_z \equiv -\bar{n}_{x'} \sin \psi \approx (\gamma H_{\text{eff}})^2 n_{x'} \sin \psi.
\]

With Eq. (14) this yields

\[
\bar{n}_z^2 \Rightarrow (\gamma H_{\text{eff}})^4 \sin^2 \psi \left[ 1 - n_{z'}^2(t) \right]/2,
\]

and integration of Eq. (18) using \( n_{z'}(t) = \tanh(\tau) \) leads exactly to Eq. (14). For \( \alpha \gtrsim 1 \) this method shows a breakdown of Eq. (10) because of the impossibility to treat the spin-photon interaction as a perturbation.

In the Landau-Zener experimental setup, the evolution of the system described by Eq. (10) proceeds for \( \alpha \ll 1 \) in two stages, see Fig. 3. The first stage is the LZ process that provides the fraction of molecules \( P \) given by Eq. (13) in the excited states at \( t > 0 \) (the upper energy branch in Fig. 3). In the second stage these excited states decay due to the superradiance onto the lower branch in Fig. 3. According to Eq. (13), at a small sweep rate almost all molecules follow the lower energy branch, so that the corresponding radiation power is small. To produce a powerful coherent electromagnetic radiation the resonance should be crossed at a rate \( v \gtrsim \Delta^2/\hbar \). To obtain the radiation at a fixed frequency, a short longitudinal field pulse is needed to drive a crystal of molecular magnets into an excited state with \( n_{z'}(0) = - \cos \psi \) and \( n_{x'}(0) = \sin \psi \). The time evolution of this state is described by Eqs. (17) and (16), whereas the electromagnetic radiation is given by Eq. (18).

Let us now analyze limitations on the superradiance relaxation rate of Eq. (13). Firstly, the linear size of the sample \( L \) should not exceed the wave length of the emitted photons \( \lambda = 2\pi/k \), otherwise photons emitted by different molecules will be out of phase and coherence will be destroyed. A conservative estimate is

\[
kL \lesssim 1, \quad \tilde{k} = n\omega/c = n\Delta^2 + W^2/(\epsilon h)
\]

which with \( N = L^3/v_0 \) yields

\[
\Gamma \lesssim \frac{E_d}{\hbar} \frac{\Delta^2}{\Delta^2 + W^2}, \quad E_d = \frac{(S_z)g^2\mu_B^2}{v_0},
\]

where \( E_d \) is the dipole-dipole energy and \( v_0 \) is the unit-cell volume. The maximal rate \( \Gamma_{\text{max}} \sim E_d/\hbar \) and thus the maximal intensity of the electromagnetic radiation can be achieved at the resonance, \( W = 0 \).

Apart of that, our theory makes use of the weak coupling \( \alpha \lesssim 1 \) [see comment below Eq. (21)]. To work out its implications, it is convenient to rewrite Eq. (13) as

\[
\alpha = (2/3)(k_0L)^3, \quad k_0 \equiv n(\Delta^2 E_d)^{1/3}/(\epsilon h).
\]

Thus \( \alpha \lesssim 1 \) converts into \( k_0L \lesssim 1 \). The weak-coupling condition is related to the requirement that the dipole-dipole interaction is sufficiently weak to prevent the
macroscopic system from dipolar ordering at low temperature (see, e.g., [28]). In the thermodynamic limit, if the condition $E_d \lesssim \Delta$ is fulfilled, then in the ground state the pseudospins in Eq. (20) point in the $x$ direction instead of ordering along the $z$ axis, as favored by the DDI. One can see that at the border of the macroscopic region, $kL \simeq 1$, Eq. (23) yields exactly $\alpha \approx 1$ for $E_d \simeq \Delta$ and $W = 0$. For $E_d \lesssim \Delta$ the weak-coupling condition $k_0L \lesssim 1$ is less restrictive than the coherence requirement $kL \lesssim 1$ that leads to the maximal rate of Eq. (22). If $\Delta \lesssim E_d$, then, at resonance, the condition $k_0L \lesssim 1$ is more restrictive than $kL \lesssim 1$, and the estimation $\Gamma_{\text{max}} \sim E_d/\hbar$ becomes invalid. Note, however, that for small tunnel splittings $\Delta$, both $k$ (at resonance) and $k_0$ are small and thus both conditions are fulfilled for realistic $L$.

For Mn$_{12}$ in the transverse field $H_x = 6$ T, so that $\langle S_x \rangle_0 = 0.777S$ and $\Delta/\hbar = 2 \times 10^{-9}$ s$^{-1}$ ($\Delta/kB \simeq 0.15 K > E_d/kB \simeq 0.04 K$), Eq. (14) with $g = 2$, and $n = 1$ gives $\alpha \approx N \times 1.9 \times 10^{-22}$. Taking $N = L^3/v_0$ with the linear size of the crystal is 0.5 cm and the unit-cell volume $v_0 = 3.7 \times 10^{-2} cm^3$ for Mn$_{12}$, one obtains $N = 3.4 \times 10^{19}$ and $\alpha \approx 0.0063$. Then Eq. (13) gives $\Gamma \approx 2.5 \times 10^8$ s$^{-1}$. For a single crystal of Mn$_{12}$, the maximal possible superradiance rate given by Eq. (22) is $\Gamma_{\text{max}} \approx 7 \times 10^9$ s$^{-1}$. For $\Delta/kB \approx 0.15 K$ this rate is achieved at $L \approx 1/k \approx 1.5$ cm which is rather large. In this case $\alpha \approx 0.17$, and the weak-coupling approximation should still be applicable. For the crystal size $L \lesssim 0.5$ cm, the maximal rate corresponds to the emission of photons of frequency $f = \omega/(2\pi) \approx 10$ GHz, i.e., $\Delta/kB \approx 0.46 K$. Similar estimations could be done for Fe$_8$ which is a better candidate for observing superradiance since in Fe$_8$ the hyperfine interactions that may cause decoherence are weak [15]. Taking for Fe$_8$ $v_0 = 2.0 \times 10^{-2}$ cm$^3$, one obtains $\Gamma_{\text{max}} \approx 1.3 \times 10^{10}$ s$^{-1}$. We have to stress that superradiance can be observed for much smaller tunnel splittings $\Delta$ than we used in the estimations above, with accordingly lower relaxation rates. The only lower limitations on $\Delta$ are that (i) it has a narrow distribution throughout the crystal and (ii) $\Gamma$ of Eq. (15) exceeds the rates of various incoherent decay processes.

In conclusion, we have demonstrated that crystals of molecular nanomagnets can exhibit superradiance in the broad frequency range. Our theory is based upon fundamental electromagnetics of a large spin and is insensitive to the details of the crystal structure as long as the spectrum of molecular spin levels consists of narrow lines determined by the crystal field and/or external magnetic field. Experimentalists should, therefore, focus on large single crystals of weakly interacting molecular magnets with weak hyperfine interactions.

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