Field-dependent superradiant quantum phase transition of molecular magnets in microwave cavities

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Abstract
We study a superradiant quantum phase transition in the model of triangular molecular magnets coupled to the electric component of a microwave cavity field. The transition occurs when the coupling strength exceeds a critical value, $d_c$, which, in sharp contrast to the standard two-level emitters, can be tuned by an external magnetic field. In addition to emitted radiation, the molecules develop an in-plane electric dipole moment at the transition. We estimate that the transition can be detected in state-of-the-art microwave cavities if their electric field couples to a crystal containing a sufficient number of oriented molecules.

Keywords: molecular magnets, quantum optics, quantum computing

(Some figures may appear in colour only in the online journal)

1. Introduction

The superradiant phase of a collection of emitters coupled to a common electromagnetic field mode is characterized by a finite number of photons in the ground state of the combined system. In the model of two-level emitters coupled to a single cavity mode [1–4], the superradiant phase appears when the emitter-field coupling $g$ exceeds some critical value $g_c$ [5, 6]. Theoretical and experimental search for the superradiant phase transition has included atoms and molecules coupled to single- and multimode optical cavities, Josephson junction qubits in microwave resonators, as well as ultracold atoms in optical traps [7–11].

According to the no-go theorem [12–14], the ground state of any collection of two-level emitters with dipolar coupling to a mode of electromagnetic field does not contain cavity photons. This result seems to render the superradiant quantum phase transition impossible, and it was extended to the case of many electromagnetic field modes and many levels in Josephson junctions [13, 14]. However, the superradiant phase transition was predicted to occur in the interacting emitters as well as in an ensemble of inhomogeneously coupled emitters and many modes [7, 15]. It was indeed observed in ultracold gases [9]. Here, we consider emission from an ensemble of interacting spins, and we are not aware of any extension of the no-go theorem that applies to our case.

Two-level emitters interacting with the quantized electromagnetic field of resonant cavity are described by the standard Dicke, Jaynes–Cummings, and Tavis–Cummings models of quantum optics [2]. Motivated by the spin-electric coupling of molecular magnets [16], we introduce a new model for the emitter in a cavity. The emitter degree of freedom represents the chirality of ground-state spin texture in a triangular molecular magnet, which interacts with the molecule’s total spin. A crystal with oriented molecular...
magnets in a strip-line cavity is then described by a generalization of the Dicke model, see figure 1.

Molecular magnets are molecules with strong exchange interaction and pronounced spin anisotropy in the low-energy sector. At low energies they can be described as a set of interacting spins localized at positions of magnetic centers. The strong anisotropy governs the relaxation from spin-1/2 to spin-1/2 due to the chirality of their spin textures. The operators \( \{C_{ij}\} \) are two-spin operators that, in analogy with the Pauli spin operators, flip the chirality \( C_{ij} \), which is a three-spin operator [16]. The operators \( S \) and \( C \) are independent and satisfy spin commutation relations: \([S_i, S_j] = i\epsilon_{ijk}S_k\), \([C_i, C_j] = i\epsilon_{ijk}C_k\), and \([S_i, C_j] = 0\), where \( i, j, \) and \( k \) count the Cartesian components of spin and chirality [16, 33].

2. Model

At low energy, triangular molecular antiferromagnets are characterized by the total spin, \( S = \sum_i S_i \), where \( i \) counts the spins-1/2 on magnetic centers, and pseudospin-1/2 chirality \( C \), associated with the spin texture, see figure 1. The components of the chirality are defined in terms of spin operators as

\[
C_i = -\frac{1}{3}(s_i \cdot s_2 - 2s_2 \cdot s_3 + s_3 \cdot s_i),
\]

\[
C_y = \frac{1}{3}(s_i \cdot s_2 - s_3 \cdot s_i),
\]

\[
C_z = \frac{1}{8\sqrt{2}}s_i \cdot (s_2 \times s_3).
\]

The components \( C_i \) and \( C_y \) are two-spin operators that, in analogy with the Pauli spin operators, flip the chirality \( C_z \), which is a three-spin operator [16]. The operators \( S \) and \( C \) are independent and satisfy spin commutation relations: \([S_i, S_j] = i\epsilon_{ijk}S_k\), \([C_i, C_j] = i\epsilon_{ijk}C_k\), and \([S_i, C_j] = 0\), where \( i, j, \) and \( k \) count the Cartesian components of spin and chirality [16, 33]. Strong antiferromagnetic exchange between the magnetic field of the molecules, and lies in the different chiralities, represented by the wavy lines. The angle \( \delta = \theta_{-1/2} - \theta_{1/2} \) determines the coupling strength of different transitions.

Figure 1. Geometry of a crystal of molecular magnets in a microwave cavity and external magnetic field. Electric field of the cavity mode is in the plane of the molecule \((x-y)\), as shown on the top panel. External magnetic field \( B \) produces the effective fields \( b = \hat{s}_{\text{mol}} \mu_B B \), which is tilted by the angle \( \psi \) from the normal \( e_z \) to the plane of the molecules, and lies in the \( x-z \) plane. The fields \( b(\pm1/2) \) form angles \( \theta_{1/2} \) with the \( z \)-axis, and define quantization axes of spin, as shown on the bottom left panel and described in the main text. On the bottom right panels, the effective quantization axes of the states with energies \( E_{C_{\pm}} \) are illustrated by arrows. The cavity field induces transitions between the states of equal spins and different chiralities, represented by the wavy lines. The angle \( \delta = \theta_{-1/2} - \theta_{1/2} \) determines the coupling strength of different transitions.
molecular spins constrains the total spin of the molecule to \( S = 1/2 \). This model is valid at the temperatures below the gap to excited \( S = 3/2 \) states, typically of the order of 10 K in spin triangles [34].

The two degrees of freedom, \( S \) and \( C \), couple differently to external fields: while the spin couples to the magnetic field via Zeeman term, the chirality couples to \( E_{\text{ph}} \), the components of external electric field in the plane of the triangular molecule [16]. The Hamiltonian of the molecular magnet in external electric and magnetic fields is [16]

\[
H_{\text{mol}} = 2\Delta_{SO} C_z S_z + b \cdot S + d_0 E_0 \cdot C.
\]  

(4)

The Bohr magneton, \( \mu_B \), and the molecular gyromagnetic ratio, \( g_{\text{mol}} \), are absorbed in the effective magnetic field \( b = g_{\text{mol}} \mu_B B \), and we set \( \hbar = 1 \). The zero-field splitting, \( \Delta_{SO} \), caused by the spin–orbit interaction and with a typical strength \( \Delta_{SO}/(g\mu_B) \sim 1 \) T, produces an Ising coupling between \( S_z \) and \( C_z \), with the \( z \)-axis normal to the molecule’s plane [17, 34]. The chirality interacts with the in-plane components of the electric field and, through the Ising coupling, with \( S \), the total spin [16, 33]. The selection rules for electrically driven transitions in equation (4) are set by the \( D_{\text{th}} \) symmetry of the molecule, and read \( \Delta C_z = \pm 1 \). Therefore, it is possible to access the transitions that would be forbidden by the selection rules \( \Delta S_z = \pm 1 \) which are valid for the magnetic driving [33].

A crystal of \( N \) emitters interacting with a mode of the resonant cavity is described by

\[
H = H_{\text{cav}} + \sum_j H_{0,j} + \sum_j V_j,
\]  

(5)

where \( H_{\text{cav}} = \omega a^\dagger a \) describes the cavity photon, and each \( H_{0,j} = 2\Delta_{SO} C_j S_j + b \cdot S \) describes a molecule interacting with an external classical magnetic field \( B \). The interaction terms

\[
V_j = d(a + a^\dagger)C_j x,
\]  

(6)

are couplings of molecules to the electric component of quantized cavity field. The operator \( a (a^\dagger) \) annihilates (creates) a cavity photon. The coupling constant \( d = d_0 E_0 \) includes both the intrinsic single-molecule spin–electric coupling \( d_0 \) and the in-plane electric field amplitude \( E_0 \). The molecules lie in a crystal lattice in parallel planes, so that their spin quantization axes all point in the same direction [35] which we label \( z \), see figure 1. Any variation of molecular orientations, e.g., due to crystal defects, is equivalent to a change in the effective coupling between the molecular spins and the cavity photons. We assume that the Zeeman coupling of \( S \) to the magnetic component of the cavity field is weak, as in the microwave cavities with molecules placed near the maximum of the electric field amplitude [36], and do not include it in equation (5).

The non-interacting Hamiltonian, \( H_0 = H_{\text{cav}} + \sum_j H_{0,j} \), conserves the number of photons \( \hat{n} = a^\dagger a \), as well as the \( z \)-components of chiralities, \( C_j z \). Within each simultaneous eigenspace of \( \hat{n} \) and \( C_j z \) it reduces to a spin Hamiltonian

\[
H_{0,j,n,c} = n\omega + b \cdot S_j + 2c\Delta_{SO}S_jz,
\]  

(7)

where \( n \) and \( c \) are the respective eigenvalues of the operators \( \hat{n} \) and \( C_j z \). This reduced Hamiltonian is readily diagonalized, and we find the energies

\[
E_{n,c,z} = j(b|c) + n\omega
\]  

and the eigenstates

\[
|n, c, s\rangle = |n, c\rangle \otimes |S \cdot e_c = s\rangle.
\]  

(9)

The effective magnetic fields are \( b|c) = b + 2c\Delta_{SO}e_c \), with \( c = \pm 1/2 \), and \( s = \pm 1/2 \) denotes the molecule’s spin projection along \( e_c \), the direction of effective field \( b|c \). Explicitly, the molecule’s eigenspaces in the \( C_j z, S_z \) basis are given by the unitary transformation \( |n, c, s\rangle = |n\rangle \otimes U(c, s) \), where \( U = \sum_{c=s=\pm 1/2} P_c \exp(-i\psi S_z) P_c \) maps the state \( |c, s\rangle \) of the molecule with chirality \( c \) and spin projection \( s \) to the \( z \)-axis into a state with the same chirality and the spin projection \( s = s_z \) along the rotated spin axis (see figure 1). The angles \( \theta_{c, s_z} \) are

\[
\theta_c = \arccos \frac{2c\Delta_{SO} + b\cos \psi}{\sqrt{b^2 \sin^2 \psi + (2c\Delta_{SO} + b\cos \psi)^2}}
\]  

(10)

with \( \psi \) and \( b \) denoting the polar angle and intensity of the field \( b \). The operators \( P_c = 2c \cdot C + 1/2 \) are projectors to the states of a given chirality \( c \).

### 3. Rotating wave approximation (RWA)

As opposed to the standard Jaynes–Cummings model in quantum optics [37], the RWA for a single-molecule magnet in a cavity cannot be obtained by simply neglecting the terms proportional to \( C \cdot a^\dagger a \) and \( C a^\dagger \), since the chirality interacts with the spin, which in addition couples to an external magnetic field.

To derive the RWA of equation (5) we switch to the interaction picture, \( V_j(t) = e^{iH_0 t} V_j e^{-iH_0 t} \), with respect to the terms \( H_0 = \sum_j H_{0,j} \) that do not involve the interaction of the molecule with the cavity electric field. Using the known eigenvalues and eigenstates of \( H_0 \), we find

\[
V_j(t) = \frac{d}{n,c,s'} \sum_{n,c,s'} e^{i(E_{n,c,s'} - E_{n,c,s})t} M(c, s, s') \times |n, c, s\rangle \langle n, c, s'| (e^{i\delta t} a^\dagger + e^{-i\delta t} a),
\]  

(11)

where \( M(c, s, s') = \langle S_j \cdot e_c = s| S_j \cdot e_c = s' \rangle \) is the scalar product of the spins with projections \( s \) and \( s' \) on the axes \( e_c \) and \( e_{-c} \). Explicitly, \( M(c, s, s) = \cos(\delta/2) \), \( M(\pm 1/2, s, -s) = \mp \sin(\delta/2) \), \( \delta = \theta_{1/2} - \theta_{-1/2} \), and the angles \( \theta_{\pm 1/2} \) are given in equation (10).

The RWA consists of neglecting the terms in the interaction-picture Hamiltonian, equation (11), that oscillate with frequencies close to molecular transitions \( \omega_n \sim |E_i - E_j| \), and keeping the terms that oscillate slowly, with frequencies close to molecular transitions.
The critical couplings in the full RWA ($d_{\text{full}}$), in standard RWA near $\omega$ ($d_{\text{res}}$), and near $\omega$ ($d_{\text{res}}$), as a function of angle with respect to the normal to molecule’s plane $\psi$, and the intensity $b$ of the external magnetic field $b$, respectively. Variations in either $\psi$ or $b$ lead the system through the superradiant quantum phase transition (motion along the arrows switches from $d > d_c$ to $d < d_c$). For this figure, the number of molecules is $N = 10^2$, and the cavity frequency is the mean of the two resonant frequencies $\omega = (\omega_1 + \omega_2)/2$ (see text). On the first panel $b = 0.9\Delta_{SO}$, and on the second $\psi = 0.6$ rad.

The condition for the validity of the RWA is that the molecule-cavity coupling constant $d$ is much smaller than the resonant frequencies, $d \ll \omega_{1,2}$. In addition, the RWA can reproduce the standard model of a two-level emitter when the cavity frequency is tuned close to one of the transitions and far from the other, e.g., $|\omega - \omega_1| \gg |\omega - \omega_2|$. This tuning is possible only when

$$|\omega_1^+ - \omega_1^-| \gg d.$$  

(12)

The condition in equation (12) can not be satisfied when $b \approx \Delta_{SO}e$, i.e., when the magnetic field axis is near the normal to the molecule, and the magnetic field intensity is comparable to spin-orbit splitting $\Delta_{SO}$. We will focus on the case when both resonances have to be taken into account, either due to the deliberate tuning of the cavity frequency, or due to violation of equation (12). In this case, the amplitudes of the resonant transitions vary strongly with the magnetic field, and we will see that this leads to new effects. When equation (12) is satisfied, the cavity can be tuned so that the RWA leads to the Tavis–Cummings model [3, 4], and consequently to the familiar superradiant phase transition and a single transition resonant with the cavity, see figure 2. We will label the critical couplings in approximations that keep a single transition as $d_{\text{res}}(d_{\text{res}})$.

After the removal of the counter-rotating terms and switching back to the Schrödinger picture, the molecule-cavity interaction is

$$V_{\text{RWA}} = d\sum \langle a + a^\dagger \rangle \left( \frac{\cos \phi}{2} C_{j,k} - \sin \phi S_{j,k} C_{j,k} \right) + i\langle a - a^\dagger \rangle \left( \sin \phi \frac{1}{2} S_{j,k} + \cos \phi \frac{1}{2} S_{j,k} \right) C_{j,k},$$  

(13)

The final Hamiltonian in RWA is $H_{\text{RWA}} = H_0 + V_{\text{RWA}}$, and it is analogous to the Tavis–Cummings model of two-level atoms in a resonant cavity. Similarly to the conservation of the number of excitations in the Tavis–Cummings model, $H_{\text{RWA}}$ conserves the quantity

$$N_{\text{exc}} = \hbar + \sum \langle 1 + \tilde{S}_{j,k} + 2C_{j,k} \tilde{S}_{j,k} \rangle,$$  

(14)

where $\tilde{S}_{j,k} = U|S_{j,k}|U^\dagger$, with $U$ defined above equation (10). We interpret $N_{\text{exc}}$ as the conserved number of excitations by counting molecules in the state $|c, s\rangle = |1/2, -1/2\rangle$ as zero excitations, molecules in the states $|1/2, 1/2\rangle$ as one excitation, molecules in the state $|1/2, -1/2\rangle$ as two excitations, and each cavity photon as one excitation. We choose an additive constant so that $N_{\text{exc}} = 0$ corresponds to all the molecules in the state $|1/2, -1/2\rangle$ and no photons in the cavity.

4. Superradiant quantum phase transition

We study the superradiant phase transition in the rotating wave and mean-field approximations. This amounts to substituting photon annihilation(creation) operator $a(a^\dagger)$ by their expectation value $\langle a \rangle \langle a^\dagger \rangle$ in $H_{\text{RWA}}$, thus neglecting any quantum fluctuations. This approximation is valid for large photon numbers, $n \gg 1$. The mean-field energy, $E_{\text{MF}}(\langle a \rangle)$ is the ground state energy of

$$H_{\text{RWA}}^{\text{MF}}(\langle a \rangle) = \omega \langle a \rangle^2 + \sum_j H_0j + V_{\text{RWA}}(\langle a \rangle).$$  

(15)

We find that $E_{\text{MF}}(\langle a \rangle)$ is independent of the phase of $\langle a \rangle$, which we set to be real in further discussion. The mean-field value of the annihilation operator, $\langle a \rangle_{\text{MF}}$ is, by the self-consistency condition, the value of $\langle a \rangle$ for which $E_{\text{MF}}(\langle a \rangle)$ is at a minimum. Similarly, the mean field state of the molecules is the ground state of $H_{\text{RWA}}^{\text{MF}}(\langle a \rangle_{\text{MF}})$. Without RWA, the phase of $\langle a \rangle_{\text{MF}}$ is set by the minimization requirement so that the quantity is real [38].

When the cavity is decoupled from the molecules, $d = 0$, the system is in the normal state, and $\langle a \rangle_{\text{MF}} = 0$. The superradiant phase transition means the appearance of $\langle a \rangle_{\text{MF}} > 0$ for coupling strength larger than the critical value, $d > d_c$. We analytically determine the critical coupling $d_c$ from the properties of $E_{\text{MF}}(\langle a \rangle)$. In the absence of photons, $E_{\text{MF}}(0)$ is a finite ground state energy of $N$ molecules in the ground state. For large photon numbers, the energy is dominated by the free photon term, and therefore diverges, $\lim_{n \to \infty} E_{\text{MF}} = \infty$. Furthermore, since $E_{\text{MF}}(\langle a \rangle)$ explicitly depends only on the square of its argument, $\partial_{\langle a \rangle} E_{\text{MF}}(\langle a \rangle)|_{\langle a \rangle = 0} = 0$. We determine the critical coupling as the smallest value of $d$ for which $\partial_{\langle a \rangle}^2 E_{\text{MF}}(\langle a \rangle)|_{\langle a \rangle = 0} < 0$. Together with the limiting values and the zero derivative at zero, this condition guarantees the existence of a minimum for the mean-field energy that is lower than $E_{\text{MF}}(0)$ at some finite value of $\langle a \rangle$.

The procedure of minimization applied to $H_{\text{RWA}}^{\text{MF}}$, equation (15), and using the RWA potential with both...
resonances, equation (13) gives the critical coupling
\[
d_{\text{Full}} = \sqrt{\frac{8\omega \Delta_{SO} b}{N}}. \tag{16}
\]
This \(d_{\text{Full}}\) is one of our main results, figure 2. The dependence is due to both the modification of the energy levels of \(H_0\), and to modification of the coupling constants for transitions through spin-overlap terms in equation (13). The result, equation (16) clearly cannot be explained by the usual RWA at either of the resonant frequencies, as illustrated in figure 2. The value of \((a)_{\text{MF}}\) grows as \((a)_{\text{MF}} \propto \sqrt{d - d_c}\) for \(d > d_c\), and \((a)_{\text{MF}} \propto \sqrt{N}\). We note that the mean-field approximation can be applied to the Hamiltonian equation (5) without the RWA, predicting the superradiant phase transition with the critical coupling scaled by a factor of 2 form the value in equation (16). The dependence of \(d_c\) on \(b\) allows for a controllable superradiant phase transition. Changes in \(d_c\), given by equation (16), can lead the system into or out of the superradiant phase, see figure 2. The measurement of the escaping radiation as done, for example, by using input–output theory [39], would then serve as a signature of superradiant state [9, 40–42]. Turning the tables, identifying the superradiant phase transition would allow to extract the value of the spin-electric coupling constant.

The quantum properties of escaping light can not be determined in the mean-field theory, since we assume that the radiation is in a specific classical state described by the expectation value \((a)_{\text{MF}}\). However, in the superradiant phase of the Dicke model, the emitted radiation is nonclassical in the sense that it cannot be described by a positive-definite probability distribution function [43]. We expect that there are quantum correlations of emitted light from our system, but their evaluation is beyond the scope of this work.

In addition to the nonzero photon occupation of the cavity mode, see figure 3, the transition is characterized by a change in the expectation value of the chirality. For \(d < d_c\), the molecules are in the state with \(C_{\text{ch}} = -1/2\), with zero expectation values of \(C_{\text{ch},i}\). After the transition, for \(d > d_c\), the in-plane components of chirality have nonzero expectation value, i.e., \(C_{\text{ch},i} \approx 0\) in our model. The fact that only the \(x\)-components gets a finite expectation value comes from our phase convention for \((a)\), and the form of the interaction with the electric fields [38]. The molecules develop electric dipole moments for \(d > d_c\), and the transition can be detected by the electric response, for example by measuring the spin-electric susceptibility [33], as well as by the emitted radiation, lower panels of figure 3.

5. Experimental requirements

The detection of the controllable superradiant phase transition is possible in an experiment that would monitor the escaping radiation or the electric response of the molecular magnets coupled to a cavity, as they are driven through the transition by a change in external magnetic field. The transition occurs when \(d_0 E_c > d_c\), see equation (16), and the controllable transition can be achieved for large electric field amplitude \(E_c\) and strong molecular spin-electric coupling \(d_0\). The critical coupling strength diminishes with the increasing number of molecules, \(d_c \propto N^{-1/2}\). Other parameters that influence \(d_c\) are the strength of the magnetic field required for control and the cavity frequency. Both are set by the zero-field splitting of the molecular magnet, \(\Delta_{SO} \approx g_\mu_B B \approx h\omega\). The typical value of zero-field splitting in triangular molecular antiferromagnets [34, 44] is \(\Delta_{SO} \approx 1 \text{ K} \cdot \mu_0\). Therefore, the relevant resonant frequencies lie in the microwave range, \(f = \omega/(2\pi) \approx 15 \text{ GHz}\), and the external magnetic fields needed for control are \(B \sim 1 \text{ T}\).

We take the estimate for the value of the molecular spin-electric coupling constant, \(d_0 \approx 10^{-14}\mu_0 R_0\), where \(R_0\) is the distance between the magnetic centers in the molecule from the \(ab\)-initio work [45, 46]. The corresponding numerical value of the dipole moment is \(d_0 \approx 10^{-33} \text{ Cm}\). Assuming the electric field amplitude \(E_c = \sqrt{\hbar\omega/c_1 V}\), where \(c_1\) is the resonator capacitance per unit length, and \(V\) is the mode volume, we estimate that \(E_c \approx 100 \text{ V/m}\) is achievable in narrow strip-line cavities [47], giving \(d = d_0 E_c \approx 10^{-11} \text{ eV}\). Under these conditions, the controllable superradiant phase transition will occur if the crystal coupled to the cavity electric field contains \(N > N_c \approx 10^5\) molecular magnets. Spin ensembles of comparable effective volume were coupled to microwaves by placing them on top of the resonators [48–50].

Coupling such a large number of molecules to a resonant cavity requires very dense crystals, with the intermolecular distances about 20 times shorter than typical 1 nm, i.e., the critical density \(n_c\) is four orders of magnitude too large. There are two molecular parameters that can be manipulated to relax.
this requirement, the zero-field splitting, $\Delta_{SO}$, and the intrinsic spin-electric coupling strength of a single molecule, $d_0$. Estimating the cavity electric field from a single photon energy in the mode volume implies $E_0 \propto \sqrt{\omega}$. Taking into account that the control magnetic field, $b$, the effective fields, $\tilde{b}(\pm1/2)$, and the resonant frequency, $\omega$, all scale with $\Delta_{SO}$, equation (16) implies

$$n_c \propto \frac{\Delta_{SO}}{d_0^2}.$$  

(17)

Triangular molecular magnets come in great variety, and the chemical alteration of their composition gives access to many spin Hamiltonians at low energies. The zero-field splitting can be as low as $\Delta_{SO} \approx 3 \times 10^{-2}$ K, and potentially even lower [51], with the values in V$_{15}$, Fe$_8$, and Cu$_3$ complexes in the range $10^{-2} - 1$ K [35, 51–55]. Modification of the intrinsic spin-electric coupling, $d_0$, can reduce the critical density even more. Since $n_c \propto d_0^{-2}$, and increase in $d_0$ does not affect any other experimental parameter, searching for the molecules with large $d_0$ may be the right way to achieve the proposed controllable superradiant phase transition in a laboratory. An increase in $d_0$ by a factor of 100 from the numerically predicted value [45, 46] would bring the critical density to the value of 1 nm$^{-3}$.

The magnetic field dependent critical coupling, equation (16), is found in the model that assumes an ideal cavity, zero temperature, and validity of the mean-field approach. The constraints for the realistic experiments are less stringent. The superradiant phase appears in the system’s ground state which is predominantly occupied at temperatures lower than the first molecule’s excitation, $T \ll \Delta_{SO}/k_B \sim 1$ K. The time scale of relaxation to the superradiant ground state is given by the spin relaxation time of the molecular magnet, which can be as long as a microsecond [44]. This time should be longer than the Rabi time of the collective coupling between the molecules and the field mode, i.e. there should be many Rabi oscillations before the spins relax. For $N > N_c$, this requirement is satisfied due to scaling of the Rabi frequency. In addition, the cavity decay time should be longer than the spin decay time, which would require the cavity $Q$-factor of the order $Q \sim 10^5 - 10^6$ for long spin coherence times of $\tau_s \sim 1$ µs, and less stringent $Q \sim 10^3 - 10^4$ for $\tau_s \sim 10$ ns. In superconducting stripline cavities, the external magnetic field of the order of 1 T would reduce the $Q$-factor, unless the field lies in the plane of the strips. There is a geometry that allows for the variation of the angle $\psi$ between the magnetic field $\mathbf{b}$ and the normal to triangles while keeping $\mathbf{b}$ in the plane of the superconductors. In this geometry, the triangles should lie in the plane normal to the axis of the strips. Further enhancement of $Q$-factor is possible by resonator engineering [56].

As a matter of principle, it is not necessary to use the stripline cavities, and any microwave resonator with large regions of significant electric field and sufficient $Q$-factor can support the superradiant phase transition. Manipulation of the electric field amplitude of the cavity mode and choosing a shape that can accommodate many molecules can be an efficient way to reach the required coupling strength, since $N_c \propto E_0^2$. Therefore, 3D cavities can also be used.

The disorder in the molecule’s energies due to imperfections of the crystal may bring some of the molecules out of resonance and reduce the effective $N$ below the total number of molecules. However, the superradiant effect also suppresses such inhomogeneous broadening [57–59]. When the collective coupling of many emitters exceeds the bandwidth of their ensemble, the broadening vanishes altogether so that even far off-resonant molecules interact strongly with the field mode. This allows one to increase the number of active emitters in the cavity in realistic devices.

6. Conclusions

We have introduced a model of a crystal of single-molecule triangular antiferromagnets interacting with an external classical homogeneous magnetic field and the electric component of a quantized cavity field. The model shows a superradiant quantum phase transition with the critical coupling tunable by applied magnetic field. The strong coupling regime is characterized by nonzero mean photon number and electric dipole moment in the triangle plane. With state-of-the-art cavities and current estimates of spin-electric coupling strength, the tunable transition is achievable for $10^5$ molecules coupled to the cavity. This value can be reduced by choosing the molecules with weak zero-field splitting $\Delta_{SO}$ and strong intrinsic spin-electric coupling $d_0$. Observation of the predicted transition and its magnetic field dependence can serve as a probe of spin-electric interaction. While our models describes triangular single-molecule magnets, it can be extended in order to study of other emitters described by entangled discrete degrees of freedom.

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