Spintronics with magnetic nanomolecules and graphene flakes

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Abstract

We show how the magnetization of nano-objects can be efficiently regulated. Several types of nanosystems are considered: magnetics nanomolecules, magnetic nanoclusters, polarized nanomolecules, and magnetic graphene. These nano-objects and the structures composed of them enjoy many common properties, with the main difference being in the type of particle interactions. The possibility of governing spin dynamics is important for spintronics.

Keywords: Magnetic nanomolecules; Magnetic nanoclusters; Polarized nanomolecules; Magnetic graphene; Spintronics

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1 Introduction

Several types of nano-objects possess magnetic moments. For instance, these are magnetic nanomolecules having a finite spin polarization in their ground state [1–4]. The typical size of a nanomolecule is 1 nm. In the ground state, magnetic nanomolecules have spins $S \sim 1/2 - 27/2$ that are frozen below the blocking temperature $T_B \sim 1 - 10$ K. Magnetic nanoclusters, formed by magnetic atoms, are very similar to magnetic molecules [3–11]. The typical sizes of such nanoclusters are defined by the coherence radius $R_{coh} \sim 1 - 10$ nm, sometimes up to $R_{coh} \sim 100$ nm. Below the blocking temperature $T_B \sim 10 - 100$ K, the magnetization is frozen. Magnetic nanoclusters can contain a large number of atoms $N \sim 100 - 10^5$, which defines large values of their spins $S \sim 100 - 10^5$. Note that nanoclusters of the size smaller than the coherence radius behave as a single magnetic molecule. But if the size is larger than the coherence radius, a nanocluster separates into several magnetic domains with opposite magnetization making the total spin zero. There also exists a class of nanomolecules containing a large number of hydrogen atoms, whose protons can be polarized. Examples are propanediol, butanol, ammonia, and many biological molecules. Systems of such molecules, although having no polarization in their ground state, but can be polarized and at low temperatures can sustain polarization for very long time [3, 4, 12, 13]. Recently, there has appeared a novel class of nanomaterials that can possess magnetic moments. These are graphene flakes, graphene ribbons, and carbon nanotubes with defects [14–16].

The possibility of efficiently regulating spin dynamics and governing spin directions is important for quantum information processing and different applications in spintronics. It is admissible to influence spin motion by transverse external fields or laser beams. In the present paper, we consider a principally different method based on the existence of a feedback field caused by the coupling of a magnetic sample with a resonant electric circuit. This way serves as the easiest mechanism of regulating spin dynamics and provides the fastest method for realizing spin reversal.

2 Resonant electric circuit

The sample, containing magnetic particles, with magnetic moment $\mu_0$, is inserted into a magnetic coil of $n$ turns, length $l$, and volume $V_c$. The coil is a part of an electric circuit, with capacitance $C$, induction $L$, and resistance $R$. The coil axis is along the axis $x$. Electric current in the circuit is defined by the Kirchhoff equation

$$L \frac{dj}{dt} + Rj + \frac{1}{C} \int_0^t j(t) \, dt = - \frac{d\Phi}{dt},$$

where the current $j$ is generated by the magnetic flux

$$\Phi = \frac{4\pi n}{cl} M_x,$$

caused by the $x$-component of the magnetization

$$M_x = \mu_0 \sum_{j=1}^{N} \langle S^x_j \rangle.$$
The electric current in the coil creates magnetic field directed along the axis $x$ and having the magnitude
\[ H = \frac{4\pi n}{cl} j \] characterized by the feedback equation
\[ \frac{dH}{dt} + 2\gamma H + \omega^2 \int_0^t H(t') \, dt = -4\pi \frac{dm_x}{dt} , \] where $\omega$ is the circuit natural frequency and $\gamma$ is the circuit damping,
\[ \omega \equiv \frac{1}{\sqrt{LC}} , \quad \gamma \equiv \frac{R}{2L} . \] The electromotive force in the right-hand side is produced by the moving magnetization density
\[ m_x \equiv \frac{M_x}{V_c} = \frac{\mu_0}{V_c} \sum_{j=1}^N \langle S^x_j \rangle , \] with $V_c$ being the coil volume.

The sample is subject to an external magnetic field $B_0$ directed along the axis $z$. Thus, the total magnetic field, acting on the sample, is
\[ B = He_x + B_0e_z . \]

The external magnetic field defines the Zeeman frequency
\[ \omega_0 \equiv \frac{|\mu_0 B_0|}{\hbar} . \] The electric circuit is called a resonator, since its natural frequency is tuned close to the Zeeman frequency, so that the resonance condition
\[ \frac{|\Delta|}{\omega} \ll 1 \quad (\Delta \equiv \omega - \omega_0) \] be valid.

### 3 Magnetic nanomolecules and nanoclusters

A system of $N$ magnetic nanomolecules or magnetic nanoclusters is described by the Hamiltonian
\[ \hat{H} = \sum_i \hat{H}_i + \frac{1}{2} \sum_{i \neq j} \hat{H}_{ij} . \] Here the single-molecule Hamiltonian is
\[ \hat{H}_i = -\mu_0 \mathbf{B} \cdot \mathbf{S}_i - D_1 (S^z_i)^2 + D_2 (S^x_i)^2 + D_4 \left[ (S^x_i)^2 (S^y_i)^2 + (S^y_i)^2 (S^z_i)^2 + (S^z_i)^2 (S^x_i)^2 \right] , \]
in which $S_i^\alpha$ is a spin-operator component of an $i$-th molecule and $D$, $D_2$, and $D_4$ are anisotropy parameters. The molecular interactions are of dipolar origin, with the interaction Hamiltonian

$$\hat{H}_{ij} = \sum_{\alpha\beta} D_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta,$$

in which

$$D_{ij}^{\alpha\beta} = \frac{\mu_0^2}{r_{ij}^3} \left( \delta_{\alpha\beta} - 3n_{ij}^\alpha n_{ij}^\beta \right)$$

is the dipolar tensor and

$$r_{ij} \equiv |\mathbf{r}_{ij}|, \quad n_{ij} \equiv \frac{\mathbf{r}_{ij}}{r_{ij}}, \quad \mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j.$$

Suppose that the system has been polarized and placed in an external magnetic field with the direction opposite to the equilibrium state. This means that the sample is prepared in a strongly nonequilibrium initial state. When no pushing transverse field is imposed, the spin motion is triggered by spin waves \cite{4,17,18}. Note that spin waves can be well defined for arbitrary nonequilibrium states \cite{19}.

Sometimes, one discusses the possibility of two other triggering mechanisms, thermal noise in the coil and photon exchange between moving spins. First, let us evaluate the influence on the spin motion of the coil thermal noise. The characteristic thermal time, required for the thermal noise to start moving spins \cite{4} is

$$t_T = \frac{4\hbar \gamma V_c}{\mu_0^2 \omega} \tanh \left( \frac{\omega}{2\omega_T} \right),$$

where

$$\omega_T \equiv \frac{k_B T}{\hbar}$$

is the thermal frequency. When the latter is larger than the resonator natural frequency, then the thermal time is

$$t_T \simeq \frac{2\hbar \gamma V_c}{\mu_0^2 \omega_T} \left( \frac{\omega}{\omega_T} \ll 1 \right).$$

The coupling of the magnet with the coil induces the coupling attenuation

$$\gamma_c = \pi \mu_0^2 N S \frac{V_c}{\hbar},$$

due to the coil feedback field. Therefore the influence of the coil on spins arises after the coupling time that can be evaluated as

$$t_c \equiv \frac{1}{\gamma_c} = \frac{\hbar V_c}{\pi \mu_0^2 N S}.$$

The ratio of the thermal to coupling times becomes

$$\frac{t_T}{t_c} \approx \frac{2\pi \gamma_c}{\omega_T} N S.$$
For magnetic nanomolecules and nanoclusters, the thermal time is much longer than the coupling time, hence thermal noise does not play role for initiating spin motion. For instance, at $T = 1 \, \text{K}$, we have $\omega_T \sim 10^{12} \, \text{s}^{-1}$. Then the thermal noise could be important only either for a small number of molecules or for small spin values, such that $2\pi\gamma NS \ll 10^{12}$. Thus, if $\gamma \sim 10^{10} \, \text{s}^{-1}$, then it should be $NS \ll 20$. Although for small number of low-spin particles, the thermal noise could play role [20], but for magnetic nanomolecules with $S \sim 10$ and moreover for magnetic nanoclusters with $S \sim 100 - 10^{5}$, thermal noise is not able to influence spin motion even for a single particle.

The other mechanism that sometimes is assumed to be present in collectivizing the rotational motion of spins in a solid-state system is the Dicke effect caused by the photon exchange between moving spins, similarly to the developing coherence and superradiance in an ensemble of radiating atoms [21] or ions [22]. Moving spins really represent dipole emitters of photons [23, 24], with the natural width

$$\gamma_0 = \frac{2\mu_0^2 S k^3}{3\hbar} \left( \frac{k}{c} \right).$$

The moving spins could induce mutual correlations in the spin motion after the typical radiation time

$$t_{\text{rad}} \equiv \frac{1}{\gamma_0} = \frac{3\hbar}{2\mu_0^2 S k^3}.$$  \hspace{1cm} (18)

However, for magnetic nanomolecules or nanoclusters, in the magnetic field $B_0 = 1 \, \text{T} = 10^4 \, \text{G}$, we have $\omega_0 \sim 10^{11} \, \text{s}^{-1}$. Then this radiation time is extremely long, being of order $t_{\text{rad}} \sim 10^8 \, \text{s} \sim 10 \, \text{years}$. On the other hand, the dephasing time due to dipolar forces is

$$T_2 \equiv \frac{1}{\gamma_2} = \frac{\hbar}{\rho \mu_0^2 S},$$ \hspace{1cm} (19)

where $\rho \sim a^{-3}$ is the density of spins, with $a$ being the mean interspin distance. For nanoclusters, with $\rho \sim 10^{20} \, \text{cm}^{-3}$ and $S \sim 10^3$, the dephasing time is $T_2 \sim 10^{-10} \, \text{s}$. The radiation time, related to photons, is incomparably longer than the dephasing time,

$$\frac{t_{\text{rad}}}{T_2} = \frac{3\rho}{2k} \gg 1,$$ \hspace{1cm} (20)

being of order $10^{18}$ and making the correlations due to photon exchange absolutely irrelevant for spin systems [24,25].

The motion of spins in magnets is triggered by spin waves and mutual correlations can be induced only by the resonator feedback field [3,4,24,25]. The amplifying role of the resonator is called the Purcell effect [26]. Such an amplification is known in the case of magnetic resonance [12,13,27].

The anisotropy parameters for nanoclusters, such as Co, Fe, and Ni, as compared to $\gamma_2 \equiv 1/T_2$, are

$$\frac{D}{\hbar \gamma_2} \sim 10^{-3}, \quad \frac{D_2}{\hbar \gamma_2} \sim 10^{-3}, \quad \frac{D_4}{\hbar \gamma_2} \sim 10^{-10}.$$

We have accomplished numerical investigation of spin dynamics for a system of many spins and for separate spins. For spin systems, we consider the average spin polarizations,
such as the $z$-polarization
\[ s \equiv \frac{1}{NS} \sum_{j=1}^{N} \langle S_z^j \rangle . \]
The spin dynamics of a single nanocluster ($N = 1$) as a function of dimensionless time, measured in units of $1/\gamma_2$, is represented in Fig. 1, where the notation $h \neq 0$ implies the presence of a resonator producing the feedback field $h \equiv \mu_0 h/\gamma_c$, while the notation $h = 0$ means the absence of the resonator. As it should be, there is no spin reversal without a resonator. While in the presence of the resonator there occurs a very fast spin reversal during the reversal time $t_{rev} \sim 10^{-10}$ s. Since, for a single nanocluster, there are no spin waves, the initial spin motion is triggered by a weak transverse magnetic field.

For many nanoclusters or nanomolecules, the reversal time becomes even shorter, reaching $t_{rev} \sim 10^{-12}$ s. One of the main differences between nanomolecules and nanoclusters is in the following. Nanoclusters cannot be prepared being identical in their sizes and spin values. While nanomolecules of the same chemical structure are identical with each other and can form perfect crystalline lattices. However, the nonuniformity of nanoclusters does not preclude the possibility of their spin correlations by the resonator feedback field [28].

4 Magnetic graphene flakes

A novel interesting nanomaterial, enjoying magnetic properties, is graphene with defects, which can be in the form of graphene flakes, graphene ribbons, and carbon nanotubes with defects [14–16]. Spins are located at defects that can be of various nature. The principal difference of such a magnetic graphene from the case of magnetic nanomolecules and nanoclusters is in the nature of spin interactions. In magnetic graphene, spins interact with each other by exchange interactions, so that the Hamiltonian reads as
\[ \hat{H} = -\mu_0 \sum_{j=1}^{N} \mathbf{B} \cdot \mathbf{S}_j + \frac{1}{2} \sum_{i \neq j}^{N} \hat{H}_{ij} , \] (21)
where the exchange interactions have the anisotropic Heisenberg form
\[ \hat{H}_{ij} = -J_{ij} (S_i^x S_j^x + S_i^y S_j^y) - I_{ij} S_i^z S_j^z . \] (22)

Since there are a number of ways for creating magnetic defects in graphene, the interaction parameters can be varied [14–16]. The governing of spin dynamics is realized similar to the case of nanomolecules and nanoclusters. The physics of the processes is also similar. We study a graphene flake prepared in a strongly nonequilibrium initial state, with the spin polarization opposite to the equilibrium direction in an external magnetic field. Magnetic defects are located on a zigzag edge of graphene. Up to 100 defects are considered. The spin motion is triggered by spin waves and collectivized by the resonator feedback field. Because of the developed coherence in spin motion, the spin reversal happens in short time of order $t_{rev} \sim 10^{-11}$ s.

We investigate the spin dynamics of defects in graphene for different parameters of the anisotropy
\[ \alpha \equiv \frac{I_{ij}}{J_{ij}} , \] (23)
where the nearest-neighbor interactions are taken, for different coupling parameters

\[
\beta \equiv \frac{\hbar \gamma_c}{\pi \omega_0} = \left| \frac{\mu_0 N S}{B_0 V_c} \right| ,
\]

under the resonator quality factor

\[
Q \equiv \frac{\omega}{2 \gamma} .
\]

Figure 2 demonstrates the behavior of the average spin polarizations \(e_x\) and \(e_z\), defined as

\[
e_{\alpha} \equiv \frac{1}{NS} \sum_{j=1}^{N} \langle S_{j}^{\alpha} \rangle \quad (\alpha = x, z),
\]

for different magnitudes of the magnetic anisotropy. As is seen, the larger the magnetic anisotropy, the longer the reversal time. Figure 3 shows the spin polarizations for the same parameters, as in Fig. 2, except for the interaction range that is taken to connect not merely the nearest neighbors, but 3 neighbor shells. The increasing interaction radius influences the most the sample with a strong magnetic anisotropy.

5 Conclusion

We have studied spin dynamics for several types of nanomaterials: magnetic nanomolecules, magnetic nanoclusters, and magnetic graphene flakes. In the latter, localized magnetic moments arise because of incorporated defects. The difference between magnetic nanomolecules or nanoclusters and magnetic graphene is in their magnetic interactions. Magnetic nanomolecules and nanoclusters interact with each other through dipolar forces, while magnetic defects in graphene exhibit exchange interactions.

For all types of magnetic samples, we consider a similar setup. The system is initially prepared in a strongly nonequilibrium state, with a magnetization opposite to the equilibrium one, in the presence of an external magnetic field. The sample is inserted into a magnetic coil of a resonant electric circuit. When there are no transverse external fields, the spin motion is triggered by spin waves. The collective dynamics develops because of the resonator feedback field. The influence of a resonator on spin motion is what is termed the Purcell effect. Coherent spin motion arises due to the Purcell effect. While the Dicke effect of interactions through the photon exchange plays no role for spin systems. The resonator thermal noise can influence spin dynamics only for small number of low-spin assemblies. But for large spin systems, as well as for nanomolecules or nanoclusters with high spins, the resonator thermal noise also is not important.

By varying the parameters of the resonant electric circuit and external magnetic fields, it is possible to realize efficient manipulation of spin dynamics, which can be used in various applications of spintronics, such as magnetic data storage and data processing \[29\]. The considered mechanism for the fast regulation of spin dynamics can also be employed for biological molecules and magnetotactic bacteria \[30\].
References

[1] Kahn, O.: Molecular Magnetism. VCH, New York (1995)

[2] Barbara, B., Thomas, L., Lionti, F., Chioresku, I., Sulpice, A.: Macroscopic quantum tunneling in molecular magnets. J. Magn. Magn. Mater. 200, 167–182 (1999)

[3] Yukalov, V.I.: Superradiant operation of spin masers. Laser Phys. 12, 1089–1103 (2002)

[4] Yukalov, V.I., Yukalova, E.P.: Coherent nuclear radiation. Phys. Part. Nucl. 35, 348–382 (2004)

[5] Kodama, R.H.: Magnetic nanoparticles. J. Magn. Magn. Mater. 200, 359–372 (1999)

[6] Hadjipanays, G.C.: Nanophase hard magnets. J. Magn. Magn. Mater. 200, 373– (1999)

[7] Werndorfer, W.: Classical and quantum magnetization reversal studied in nanometer-sized particles and clusters. Adv. Chem. Phys. 118, 99–190 (2001)

[8] Ferre, J.: Dynamics of magnetization reversal: from continuous to patterned ferromagnetic films. Adv. Chem. Phys. 83, 127–185 (2002)

[9] Bedanta, S., Kleemann, W.: Supermagnetism. J. Phys. D 42, 013001 (2009)

[10] Berry, C.C.: Progress in functionalization of magnetic nanoparticles for application in biomedicine. J. Phys. D 42, 224003 (2009)

[11] Beveridge, J.S., Stephens, J.R., Williams, M.E.: The use of magnetic nanoparticles in analytical chemistry. Annu. Rev. Anal. Chem. 4, 251–273 (2011)

[12] Chen, H.Y., Lee, Y., Bowen, S., Hilty, C.: Spontaneous emission of NMR signals in hyperpolarized proton spin systems. J. Magn. Res. 208, 204–209 (2011)

[13] Krishnan, V.V., Murali, N.: Radiation damping in modern NMR experiments: progress and challenges. Prog. Nucl. Magn. Res. Spectrosc. 68, 41–57 (2013).

[14] Yaziev, O.V.: Emergence of magnetism in graphene materials and nanostructures. Rep. Prog. Phys. 73, 056501 (2010)

[15] Katsnelson, M.I.: Graphene: Carbon in Two Dimensions. Cambridge University, Cambridge (2012)

[16] Enoki, T., Ando, T.: Physics and Chemistry of Graphene. Pan Stanford, Singapore (2013)

[17] Yukalov, V.I.: Origin of pure spin superradiance. Phys. Rev. Lett. 75, 3000–3003 (1995)

[18] Yukalov, V.I.: Nonlinear spin dynamics in nuclear magnets. Phys. Rev. B 53, 9232–9250 (1996)
[19] Birman, J.L., Nazmitdinov, R.G., Yukalov, V.I.: Effects of symmetry breaking in finite quantum systems. Phys. Rep. \textbf{526}, 1–91 (2013)

[20] Kiselev, Y.F., Shumovsky, A.S., Yukalov, V.I.: Thermal-noise induced radio frequency superradiance in resonator. Mod. Phys. Lett. B \textbf{3}, 1149–1156 (1989)

[21] Allen, L., Eberly, J.H.: Optical Resonance and Two-Level Atoms. Wiley, New York (1975)

[22] Bourhill, J., Goryachev, M., Farr, W.G., Tobar, M.E.: Superradiant behavior of $Cr^{3+}$ ions in ruby revealed by whispering gallery modes. \texttt{arXiv:1504.07733} (2015)

[23] Yukalov, V.I.: Coherent dynamics of radiating atomic systems in pseudospin representation. Laser Phys. \textbf{24}, 094015 (2014)

[24] Yukalov, V.I., Yukalova, E.P.: Absence of spin superradiance in resonatorless magnets. Laser Phys. Lett. \textbf{2}, 302–308 (2005)

[25] Yukalov, V.I.: Spin superradiance versus atomic superradiance. Laser Phys. Lett. \textbf{2}, 356–361 (2005)

[26] Purcell, E.M.: Spontaneous emission probabilities at radio frequencies. Phys. Rev. \textbf{69}, 681 (1946)

[27] Davis, C.L., Kaganov, I.V., Henner, V.K.: Superradiation in magnetic resonance. Phys. Rev. B \textbf{62}, 12328–12337 (2000)

[28] Kharebov, P.V., Henner, V.K., Yukalov, V.I.: Optimal conditions for magnetization reversal of nanocluster assemblies with random properties. J. Appl. Phys. \textbf{113}, 043902 (2013)

[29] Dimian, M.: Nonlinear spin dynamics and ultra-fast precessional switching. Ph.D. Thesis, University of Maryland (2005)

[30] Wang, H., Yu, Y., Sun, Y., Chen, Q.: Magnetic nanochains. Nano \textbf{6}, 1–17 (2011)
Figure Captions

Figure 1. Spin polarization $s = s(t)$ of a single nanocluster as a function of the dimensionless time, measured in units of $1/\gamma_c$, for the parameters $\omega/\gamma_c = \omega_0/\gamma_c = 10$, $(2S-1)D/(h\gamma_c) = (2S-1)D_2/(h\gamma_c) = 1$, and small $D_4/D \sim 10^{-7}$, with $\gamma/\gamma_c = 1$. The solution in the presence of resonator (solid line) is compared with that in the absence of resonator (dashed line).

Figure 2. Transverse polarization $e_x$ (dotted line) and longitudinal polarization $e_z$ (solid line) for magnetic graphene with 100 defects on a zigzag edge as a function of dimensionless time, measured in units of $1/\omega$, for the coupling parameter $\beta = 0.01$, the resonator quality factor $Q = 10$, and different anisotropy parameters: (a) $\alpha = 1$; (b) $\alpha = 1.2$; (c) $\alpha = 1.4$. Only the nearest-neighbor interactions are assumed.

Figure 3. The same as in Fig. 2, but for interactions ranging over three neighbor shells.
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