Triggering spin reversal in nanomolecules and nanoclusters on demand

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Abstract

Spin reversal in magnetic nanomolecules and nanoclusters is considered. A method is suggested allowing, from one side, to keep for long time magnetic polarization in a metastable state and, from the other side, for starting the reversal process at any required time. This method can find applications for the operation of storage memory devices and for the regulation of processes in spintronics.

Keywords: magnetic nanomolecules, spin reversal, data storage, memory devices, triggering condition
Introduction

Magnetic nanomolecules [1–7] and nanoclusters [8,9] of different nature are of extraordinary technological importance with a myriad of applications that permeate daily life. Some properties exhibited by quantum dots, whose sizes are in the nanometer range, are similar to those of nanomolecules and nanoclusters, because of which quantum dots are often called “artificial atoms” [10]. There also exist magnetic quantum dots [11–14] enjoying some of the properties of magnetic nanomolecules and nanoclusters.

Most applications of nanomagnets involve rotating the magnetization orientation of one or more nanomagnets. A single-domain nanomagnet is a nanomagnet of sufficiently small size having a single ferromagnetic domain in which all the spins point in the same direction because of strong exchange interaction between them. That direction is the direction of its magnetization. If we rotate the magnetization, then all the spins in the single-domain nanomagnet rotate together in unison, so the magnetization acts like a giant single spin. This is called coherent rotation. If the process of coherent rotation is sufficiently fast, which can be achieved by connecting the sample to a resonance electric circuit [15], magnetic nanomolecules and nanoclusters can emit coherent radiation [16–22]. Sufficiently fast reversal of magnetization, in about $10^{-8}$ s, can be realized by acting on the sample with alternating magnetic fields [23]. Short intensive laser pulse can reverse magnetization in about $10^{-9}$ s [24]. We consider spin reversal caused by the action of resonator feedback field [16–19, 21, 22], which seems to provide the most convenient and, probably, the fastest method for spin reversal [25].

Among the most important applications of magnetic nanomolecules and nanoclusters, it is necessary to mention the possible use of their spins for data storage in memory devices, for spin-based quantum computers [26, 27], and for information processing [28]. To serve as an efficient storage memory device, the system has to satisfy two main properties contradicting each other:

(i) It can keep information for long time, which is connected with the feasibility of keeping intact the fixed spin position. This can be provided by a strong anisotropy typical of molecular magnets and clusters.

(ii) The memory can be either quickly erased or changed by reversing spin polarization. This means that the magnetic anisotropy could be suppressed at any required moment of time.

In this article, we suggest a method allowing for triggering spin reversal in magnetic nanomolecules and nanoclusters with large magnetic anisotropy at any desired time. Some trapped spin-1 atoms in optical lattices, e.g. $^{87}$Rb atoms in the $F = 1$, $m_F = -1$ hyperfine state, can also possess magnetic anisotropy [29], hence clusters of trapped atoms can also be kept in mind.

Main equations

The Hamiltonian typical of a magnetic nanomolecule or a nanocluster is

$$\hat{H} = -\mu_S \mathbf{B} \cdot \mathbf{S} + \hat{H}_A,$$

where in the Zeeman term $\mu_S = -g_S \mu_B$ is the magnetic moment of the molecule, $g_S$ the molecule Landé factor, and $\mu_B$, Bohr magneton. The second term is the Hamiltonian describing magnetic anisotropy,

$$\hat{H}_A = -D S_z^2 + E(S_x^2 - S_y^2),$$

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with the parameters

$$D = \frac{1}{2} (D_{xx} + D_{yy}) - D_{zz}, \quad E = \frac{1}{2} (D_{xx} - D_{yy}),$$

expressed through the tensor of magnetic anisotropy $D_{\alpha\beta}$.

The sample is inserted into a magnetic coil of a resonance electric circuit creating a feedback field $H$. The total magnetic field, acting on the sample,

$$B = (B_0 + \Delta B) e_z + H e_x + B_1 e_y,$$

consists of a constant field $B_0$ along the axis $z$, an additional regulated field $\Delta B$ that can be varied, the feedback field of the resonator coil, $H$ in the $x$ direction, and a small anisotropy field $H_1$ along the axis $y$.

The feedback field $H$ satisfies the equation

$$\frac{dH}{dt} + 2\gamma H + \omega^2 \int_0^t H(t') \, dt' = -4\pi \eta_f \frac{dm_x}{dt},$$

following [16–19, 25] from the Kirchhoff equation. Here $\gamma$ is the resonator attenuation, $\omega$, resonator natural frequency, $\eta_f = V/V_c$ is a filling factor, $V$ sample volume, $V_c$ coil volume, and the right-hand side is the electromotive force produced by moving spins with the magnetization density

$$m_x = \frac{\mu_s}{V} \langle S_x \rangle.$$

For what follows, let us introduce the notations for the Zeeman frequency

$$\omega_0 \equiv -\frac{\mu_s}{\hbar} B_0,$$

regulated frequency

$$\Delta \omega \equiv -\frac{\mu_s}{\hbar} \Delta B,$$

and the transverse frequency

$$\omega_1 \equiv -\frac{\mu_s}{\hbar} B_1.$$

The right-hand side of the feedback equation (4), which is the electromotive force, is proportional to the rate

$$\gamma_0 \equiv \pi \eta_f \frac{\mu_s^2 S}{hV} = \pi \frac{\mu_s^2 S}{hV_c}$$

that can be called feedback rate. It is useful to define the dimensionless feedback field

$$h \equiv -\frac{\mu_s H}{h\gamma_0}.$$

Using the commutators

$$[S_x, S_y^2] = -[S_x, S_z^2] = i(S_yS_z + S_zS_y),$$

$$[S_y, S_z^2] = -[S_y, S_x^2] = i(S_xS_z + S_zS_x),$$

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[ \mathbf{S}_z, \mathbf{S}_y^2 ] = - [ \mathbf{S}_z, \mathbf{S}_y^2 ] = i(\mathbf{S}_z \mathbf{S}_z + \mathbf{S}_z \mathbf{S}_x) ,

we derive the Heisenberg equations of spin motion for the x-component,

$$\frac{dS_x}{dt} = -(\omega_0 + \Delta \omega)S_y + \omega_1 S_z + \frac{D + E}{\hbar} (S_y S_z + S_z S_y) ,$$

for the y-component,

$$\frac{dS_y}{dt} = (\omega_0 + \Delta \omega)S_x - \gamma_0 h S_z - \frac{D + E}{\hbar} (S_x S_z + S_z S_x) ,$$

and for the z-component,

$$\frac{dS_z}{dt} = \gamma_0 h S_y - \omega_1 S_x + \frac{2E}{\hbar} (S_x S_y + S_y S_x) .$$

It is convenient to introduce the variables

$$x \equiv \frac{\langle S_x \rangle}{S} , \quad y \equiv \frac{\langle S_y \rangle}{S} , \quad z \equiv \frac{\langle S_z \rangle}{S} ,$$

varying in the interval \([-1, 1]\).

We use the decoupling of pair correlations in the form \[16, 17\]

$$\langle S_\alpha S_\beta + S_\beta S_\alpha \rangle = \left( 2 - \frac{1}{S} \right) \langle S_\alpha \rangle \langle S_\beta \rangle \quad (\alpha \neq \beta) ,$$

which is exact for spin one-half, since

$$S_\alpha S_\beta + S_\beta S_\alpha = 0 \quad (\alpha \neq \beta, \ S = \frac{1}{2}) ,$$

and for large spins \(S \rightarrow \infty\) that behave classically.

The feedback-field equation \((\ref{equation:feedback})\) becomes

$$\frac{dh}{dt} + 2\gamma h + \omega^2 \int_0^t h(t') \, dt' = 4 \frac{dx}{dt} .$$

The dimensionless anisotropy parameter

$$A \equiv \frac{\omega_D + \omega_E}{\omega_0}$$

is expressed through the effective anisotropy frequencies

$$\omega_D \equiv (2S - 1) \frac{D}{\hbar} , \quad \omega_E \equiv (2S - 1) \frac{E}{\hbar} .$$

Then equations \((\ref{equation:dx})\), \((\ref{equation:dy})\) and \((\ref{equation:dz})\) read as

$$\frac{dx}{dt} = -\omega_0(1 + b - Az)y + \omega_1 z , \quad \frac{dy}{dt} = \omega_0(1 + b - Az)x - \gamma_0 h z ,$$
\[
\frac{dz}{dt} = 2\omega_E x y - \omega_1 x + \gamma_0 h y ,
\]
where

\[
b \equiv \frac{\Delta \omega}{\omega_0} = - \frac{\mu S \Delta B}{\hbar \omega_0} .
\]  

The feedback-field equation (16) can be rewritten as the differential equation

\[
\frac{d^2 h}{dt^2} + 2\gamma \frac{dh}{dt} + \omega^2 h = 4 \frac{d^2 x}{dt^2} .
\]  

The initial conditions are

\[
x_0 = x(0) , \quad y_0 = y(0) , \quad z_0 = z(0) ,
\]
\[
h_0 = h(0) = 0 , \quad \dot{h}_0 = \dot{h}(0) = 0 ,
\]
where the overdot means time derivative.

3 Triggering condition

Let the system be prepared so that the spin be polarized along the axis \( z \) with the initial value \( z_0 > 0 \), while \( x_0 = y_0 = 0 \). This direction of spin, formed by the spins of electrons, under the magnetic field \( B_0 > 0 \), is metastable and the spin tends to reverse to the direction down. As we know \[16\]–\[19\], if the anisotropy parameter \( A \) were small, the process of spin reversal would start from the very beginning. However, in nanomolecules and nanoclusters, this parameter \( A \) can be of order one and larger. Then the spin is blocked and can stay intact during quite long time of the order of the longitudinal relaxation time \( T_1 \) due to spin-phonon interactions. This time can be estimated by the Arrhenius law

\[
T_1 = \tau_0 \exp \left( \frac{U_{\text{eff}}}{k_B T} \right) ,
\]
with \( U_{\text{eff}} \) being the effective barrier separating the directions of spin up and spin down. Depending on temperature \( T \), the relaxation time \( T_1 \) can be of the order of hours even months.

To start spin reversal, it is required that the resonance be realized, when the effective Zeeman frequency of spin rotation would be close to the resonator natural frequency \( \omega \). In our case, as equations (19) show, the effective Zeeman frequency is

\[
\omega_{\text{eff}} = \omega_0 (1 + b - Az) .
\]

Since the spin polarization \( z \) changes from \( z = 1 \) to \( z = -1 \), the effective frequency \( \omega_{\text{eff}} \) varies by a large quantity \( 2A\omega_0 \), hence no permanent resonance can be realized.

Suppose the sample is in a metastable spin state \( z_0 > 0 \), as described above, and can keep that state for very long times due to large magnetic anisotropy. Let \( \omega = \omega_0 \). The regulated field \( b = b(t) \) is a function of time. We put forward the suggestion that the reversal process can be triggered at any chosen time \( \tau \) provided the resonance is realized at this time, so that

\[
\omega_{\text{eff}}(\tau) = \omega .
\]
This implies that at the triggering time $\tau$ there should be

$$b(\tau) = A z_0 \quad (\omega = \omega_0).$$

(25)

Taking the initial spin polarization as $z_0 = 1$, we get the triggering condition

$$b(t) = \begin{cases} 0, & t < \tau \\ A, & t \geq \tau \end{cases}.$$  

(26)

4 Numerical solution

To study spin dynamics, we need to solve the system of equations (19) and (21). Before the solution, let us estimate the typical parameters entering the equations.

One of the well studied magnetic nanomolecules is the dodecanuclear manganese cluster with the chemical formula $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$, which is briefly named Mn$_{12}$. It has spin $S = 10$ and blocking temperature 3.3 K. Spin polarization can be kept frozen for very long times depending on temperature. The time $T_1$ is given by the Arrhenius law, where $\gamma_0 \sim (10^{-7} - 10^{-8})$ s. Thus at $T = 3$ K, the spin is frozen for one hour and at 2 K, for 2 months. The molecule radius is around $10^{-7}$ cm and the volume of a molecule is $V \sim 10^{-20}$ cm$^3$. The Zeeman frequency depends on the magnetic field $B_0$. Thus for $B_0 = 1T = 10^4$ G, we have $\omega_0 \sim 10^{11}$ s$^{-1}$. The feedback rate (9) is $\gamma_0 \sim 10^8$ s$^{-1}$. The anisotropy parameter $D \sim 10^{-16}$ erg, while $E$ is very small, being close to zero. Then $D/k_B \approx 0.6$ K and $D/\hbar \sim 10^{11}$ s$^{-1}$. The anisotropy frequency is $\omega_D \sim 10^{12}$ s$^{-1}$. Then the anisotropy parameter (17) is $A \sim 10$.

The other often mentioned nanomolecule is the octanuclear iron cluster, with the formula $[\text{Fe}_8\text{O}_2(\text{OH})_{12} (\text{tacn})_6]^{8+}$, where “tacn” stands for organic ligand triazacyclononane. The abbreviation for this molecule is Fe$_8$. Its properties are close to Mn$_{12}$. Spin is $S = 10$. Blocking temperature is $T_B \approx 1$ K. The molecule volume $V \sim 10^{-20}$ cm$^3$. The anisotropy parameters are $D \sim 0.4 \times 10^{-16}$ erg and much smaller $E$. Thus $D/k_B = 0.27.5$K and $E/k_B = 0.046$ K, or $D/\hbar \sim 4 \times 10^{10}$ s$^{-1}$ and $E/\hbar \sim 10^{10}$ s$^{-1}$. The anisotropy frequencies are $\omega_D \sim 4 \times 10^{11}$ s$^{-1}$ and $\omega_E \sim 10^{10}$ s$^{-1}$. Then the anisotropy parameter (17) is $A \sim 1 - 4$.

Typical parameters of Co, Fe, and Ni nanoclusters are as follows. The volume is close to $V \sim 10^{-20}$ cm$^3$, the number of atoms in a cluster is $N \sim 10^3 - 10^4$, the total cluster spin is $S \sim 10^3 - 10^4$, blocking temperature is $T_B \sim (10 - 100)$ K. For the magnetic field $B_0 \sim 1$ T, the Zeeman frequency is $\omega \sim 10^{11}$ s$^{-1}$. The feedback rate (9) is $\gamma_0 \sim (10^{10} - 10^{11})$ s$^{-1}$. The anisotropy parameters are $D \sim 10^{-20}$ erg and $E \sim 10^{-19}$ erg, which gives $D/\hbar \sim 10^7$ s$^{-1}$ and $E/\hbar \sim 10^6$ s$^{-1}$. Therefore $\omega_D \sim (10^{10} - 10^{11})$ s$^{-1}$ and $\omega_E \sim (10^9 - 10^{10})$ s$^{-1}$. Thus the dimensionless anisotropy parameter (17) is $A \sim 0.1 - 1$.

Numerical solution of equations (19) and (21) is accomplished for the initial conditions $x_0 = y_0 = 0$, $z_0 = 1$, $h_0 = 0$, and $\dot{h} = 0$. Frequency parameters are measured in units of $\gamma_0$ and time, in units of $\gamma_0^{-1}$. In the figures, the accepted parameters are: $\omega = \omega_0 = 10$, $\omega_E = \omega_1 = 0.01$, $\gamma = 1$, and $A = 1$.

In order to emphasize the importance of switching on the regulated field $b$ exactly to the anisotropy parameter $A$, in Fig. 1, we relax this requirement, by switching on the regulated field $b$ to different values $B = b(\tau)$ and show that the reversal starts exactly at the given delay $\tau$ only when $B = A = 1$. When $B$ does not equal $A$, the beginning of the reversal shifts to
times larger than $\tau$. If the regulated field is not switched on at all, hence $b = B = 0$, there is no spin reversal.

In Fig. 2, the triggering condition (26) is preserved, with $B = A = 1$, while the delay time $\tau$ is varied. As is seen, the spin reversal starts exactly at the given delay time $\tau$. The resonance condition (24) is valid at the time $\tau$, but later on, when $t > \tau$, the resonance condition (24) is not satisfied. This explains the appearance of the tails with the slower spin reversal.

Figure 3 shows the behavior of the transverse spin component $x$, when the triggering resonance, with $B = A = 1$, is switched on at the time $\tau = 10$. In Fig. 3a, the interval of time is $[0, 40]$, while in Fig. 3b, the interval is $[10, 20]$. Figure 4 displays the behavior of the feedback field $h$ for the same parameters as in Fig. 3.

## 5 Conclusion

For the operation of memory storage devices and other spintronics instruments, it is required, from one side, to have the possibility of keeping for long time a fixed spin alignment, and, from the other side, to be able to reverse the spin at any chosen moment of time. It is not a problem to block a spin for very long times using materials with large magnetic anisotropy. However, the same magnetic anisotropy does not allow for the realization of fast spin reversal. It would, of course, be possible to suppress the magnetic anisotropy by a strong external magnetic field, which, however, would need the use of very large fields, an order larger than the magnetic anisotropy. The optimal solution would be the use of minimally high magnetic fields for triggering spin reversal.

A method is advanced allowing for the initiation of spin reversal in nanomolecules and nanoclusters at any desired time. The idea of the method is to insert the sample inside a coil of electric circuit that creates a feedback field acting on spins and to arrange, at the required time, a resonance between the sample Zeeman frequency and the circuit natural frequency. This time-local resonance immediately triggers the start of spin reversal.

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Figure Captions

**Figure 1.** Longitudinal spin polarization as a function of time for $\omega = \omega_0 = 10$, $\omega_E = \omega_1 = 0.01$, $\gamma = 1$, $A = 1$, and different values of the switched on regulated field $b(\tau) = B$. The triggering resonance happens only for $B = A = 1$.

**Figure 2.** Spin polarization as a function of time for the same parameters as in Fig. 1, but with the fixed triggering resonance condition $B = A = 1$ and varying delay time $\tau$.

**Figure 3.** Transverse spin component $x$ as a function of time for the same parameters as in Fig. 1, under the fixed triggering resonance condition $B = A = 1$ and the delay time $\tau = 10$. Figure 3a shows the time interval $[0, 40]$ and 3b, the time interval $[10, 20]$.

**Figure 4.** Time dependence of the feedback field $h$ for the parameters as in Fig. 3.
Figure 1: Longitudinal spin polarization as a function of time for $\omega = \omega_0 = 10$, $\omega_E = \omega_I = 0.01$, $\gamma = 1$, $A = 1$, and different values of the switched on regulated field $b(\tau) = B$. The triggering resonance happens only for $B = A = 1$.

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