Macroscopic quantum coherent effects induced by electric current in dynamics of lanthanide based single molecule toroics

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Abstract. The dynamics of a quantum system with a large toroidal moment under the influence of a time-dependent electric current coupled with the toroidal moment is considered. The possibility of observing the quasi-anyonic excitations, the Bloch type oscillations in the precession motion of the toroidal moment, the Stark-type resonances, and the tunnel transitions between different precession modes are discussed.

1. Introduction
Recently, much attention has been drawn to investigations of physical properties of metal-organic molecules with rare-earth ion core [1, 2]. Such materials are very interesting because the ordering of magnetic ions in them is described by a toroid (anapole) moment associated to a ground state of a zero magnetic moment. This is why the building blocks of these materials are called single molecule toroics (SMTs) instead of single molecule magnets (SMMs). The most prominent and investigated are dysprosium based SMTs, from the planar molecules of Dy₃ [3], Dy₄ [4], and Dy₆ [5] to the recently synthesized cubane Dy₄ molecules [6].

The toroidal moment as a novel degree of freedom makes it possible to implement new interesting physical properties and phenomena in dynamics of such systems, for example, the possibility of observing the effect of macroscopic quantum tunneling of toroidal moment, Rabi oscillations as evidence of the existence of quantum coherence, etc. The presence of the toroidal moment also determines the possibility of observing the magnetoelectric effect, including the non-equilibrium quantum one.

These effects are essentially macroscopic coherent, since they are realized on the scale of a sample, which is (at sufficiently low temperatures) a coherent ensemble of particles that almost do not interact with each other. At the same time, predominantly one-electron mechanisms of the formation of electric dipole moments in 4f-shells of rare earth ions lead to the rather strong magnetoelectric coupling.

Versatile properties of SMTs open up new possibilities for applications, especially in the fields of quantum molecular spintronics and quantum computing. The undoubted advantage of the systems is the presence of a toroidal moment, which by its nature is well coupled with crossed electric and magnetic fields, as well as with electric currents (particle and/or displacement ones).
Thus, it is possible to control the states of SMTs by electrical means that have significant advantages over magnetic control, primarily due to better localizability.

In addition, the study of the magnetic and magnetoelectric properties of such mesoscopic objects helps to achieve better understanding the intermediary region between classical physics and quantum physics, which is one of the most intriguing fundamental problems up today.

In this work, the dynamics of a quantum system with a large toroidal moment (SMTs prototypes with rare-ion core of six or even more ions, located at the apices of regular polygons) under the influence of a time-dependent electric current interacting with a toroidal moment is considered. This interaction introduces new features into the dynamics of the SMTs. The possibility of observing the quasi-anionic excitations, the Bloch type oscillations in the precession motion of the toroidal moment, the Stark type resonances, and the tunnel transitions between different precession modes are discussed. These quantum effects manifest themselves in the form of the toroidal moment projection jumps on the corresponding curve of dependence on the external electric current.

2. The model

We consider a spin ring, a system of \( N \geq 3 \) non-Kramers rare-earth ions located at the apices of a regular polygon (see fig. 1). The Hamiltonian of the rare-earth polygonal cluster reads

\[
\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_{CF}^{(i)} + \mathcal{H}_{INT} + gJ \mu_B \sum_{i=1}^{N} H J_i,
\]

where \( \mathcal{H}_{CF}^{(i)} \) is the operator of the crystal field at the \( i \)-th ion location, \( J_i \) is the total angular momentum of the \( i \)-th ion, \( H \) is the external magnetic field strength, and \( \mathcal{H}_{INT} \) is the Hamiltonian of the dipole and exchange interactions of the rare-earth ions in the cluster.

**Figure 1.** The spin structure of a polygonal rare-earth molecular cluster and the orientation of the local easy axes. The thicker arrows represent the spins of rare-earth ions in the molecule.

The ground state of rare-earth ions in compounds is formed mainly under the influence of a crystal field and often has a strong anisotropy of the magnetic moment. For example, the ground multiplet \( ^6H_{15/2} \) of Dy\(^{3+} \) ions in a Dy\(_3\) cluster is split in such a way that the ground state is a very close Kramers doublet \(|MJ = \pm 15/2\rangle\) \([3, 7]\), which responds only to the \( z_i \) local component of an external magnetic field. The first excited state is separated from the ground state by the energy of 200 cm\(^{-1}\). The wave functions of the excited state are close to \(|MJ = \pm 13/2\rangle\). It is possible therefore to conclude that the environment of rare-earth ions is almost axially symmetric.

In the case of non-Kramers ions, small asymmetrical perturbations remove degeneration, thus making the ground state a quasi-doublet, i.e. two close singlets with a splitting that is small compared with the interval to higher levels. According to the Griffiths theorem \([9]\), the magnetic moments of the ions can be directed only along a specific axis, namely the local \( z_i \)-axes.

There are \( 2^N \) possible orderings of the ion spins in the rare-earth polygonal cluster. The wave functions of the cluster can be written as \( \chi_n = \prod_{i=1}^{N} |\sigma_{m_i}\rangle \), where \( \sigma_{m_i} \) stands for the sign (”+” or ”−”) of the projection of the spin \( i \)-th ion (\( i = 1, ..., N \)) onto the local \( z_i \) axis in the \( n \)-th state (\( n = 1, ..., 2^N \)).
The spin orderings in a molecule can be characterized in terms of spin chirality. It is clear that spins in the states $\chi_n (n = 1, \ldots, 2^N-1)$ and their conjugates $\chi_n (n = 2^N-1 + 1, \ldots, 2^N)$ are inversely twisted, i.e. the states have opposite chirality. The natural physical quantity associated with spin chirality in this case is the $T$-odd polar vector of the anapole (toroidal) moment [8].

We note that the toroidal moment operator in the case of localized magnetic ions is defined as

$$ T = \frac{1}{2} g J \mu_B \sum_{i=1}^{N} [r_i \times J_i], \quad (2) $$

where $r_i$ is the position vector of the $i$-th apex (all $r_i = r_0$).

We will use the value $T_0 = \frac{1}{2} g J \mu_B r_0 J$ as a unit of a toroidal moment ($T_0$ can be considered something like a quantum of the toroidal moment). The dimensionless quantity $T/T_0$ is formally equal to the effective "magnetization" $\sum_i \sigma_i$, associated with the effective Hamiltonian in eq. (1).

Obviously, the toroidal moment of the system in a $\chi_n$ state is $T = (q_+ - q_-) T_0$, where $q_{\pm}$ is the number of "+"s and "-"s in the $\chi_n$ state. The values of the toroidal moments for conjugate states are opposite in sign. The toroidal moment of the ground state is $T = N T_0$.

3. The current-driven dynamics

In order to consider the current-driven dynamics of the toroidal moment, it is necessary to take into account the interaction between the toroidal moment and external electric current, described by the term

$$ W = -\frac{4\pi}{c} T \cdot j(t), \quad (3) $$

where $T$ is the toroidal moment and $j(t)$ is the density of a time-dependent electric current. The current can be both particle or displacement current. This paper focuses on the quite interesting case of planar currents, i.e. currents directed along the plane of a rare-earth polygon. As a number of the apices in the rare-earth $N$-gon can be quite large, we assume that $T/T_0 >> 1$, thus the quasi-classical approach can be applied.

The convenient means to investigate the dynamics of the toroidal moment is the coherent quantum states $|\theta(t), \varphi(t)\rangle$ (for the theory on coherent quantum states, see ref. [10]). Here $\theta$ and $\varphi$ are the polar and azimuthal angles of the toroidal moment relative to the direction of the electric current. The Lagrange functions derived from the Hamiltonian (1) of the system reads

$$ L = N \hbar \left( 1 - \cos \theta \right) \dot{\varphi} - U_a(\theta, \varphi) + \frac{4\pi}{c} T j(t) \cos \theta. \quad (4) $$

The first term in this equation is the Wess-Zumino term, which reflects non-orthogonality of coherent states at different points in time, the second term $U_a(\theta, \varphi)$ gives the "anisotropy" energy,

$$ U_a(\theta, \varphi) = -N J_1 \sin^2 \theta - N J_2 \sin^2 \theta \cos 2\varphi, \quad (5) $$

where $J_1$ is the exchange interaction constant between neighbouring rare-earth ions (typical values are $10$ cm$^{-1}$). The second contribution in eq. (5) describes the splitting between the singlet levels of a rare-earth ion in the crystal field with respect to the local axes. In view of the notation uniformity, this contribution is formulated in terms of the effective exchange constant $J_2$ ($0 < J_2 << J_1$). The third term in eq. (4) is merely the Zeeman-like energy of the interaction between the time-dependent electric current and the toroidal moment.

The partition function of such a system can be written as a path integral. As exchange interaction between dysprosium ions in a molecule is strong enough and if the external current is not very large, then $\theta \approx \frac{\pi}{2}$. This gives the opportunity to perform the integration over the
θ variable and to reduce the problem to one-dimensional. The resulting Schrödinger equation reads:

\[ i\hbar \frac{\partial \psi}{\partial t} = \left( \frac{p_\varphi^2}{2J_\varphi} + U_a(\varphi) - M \varphi \right) \psi, \]

(6)

where \( p_\varphi = -i\hbar \frac{\partial}{\partial \varphi} \) is the generalized momentum operator (\( J_\varphi = N\hbar^2/8J_1 \) stands for the moment of inertia), \( U_a(\varphi) = -NJ_2 \cos 2\varphi \) is the potential energy operator, and \( M = (\pi\hbar T/J_1)(dj(t)/dt) \) can be considered as a torque.

In the case of a stationary current when \( j(t) = \text{const} \) and \( M = 0 \), eq. (6) is a well-known Mathieu equation [11]. According to the Floquet theorem (known as the Bloch theorem in physics of solids), the eigenfunctions \( \psi_n(\varphi) \) have the property

\[ \psi_n(\varphi + \pi) = e^{i\pi \tau} \psi_n(\varphi), \]

(7)

where \( \tau \) is an arbitrary real number, which plays the same role as quasi-momentum in solid-state physics. By analogy, we will call this value a toroidal quasi-moment. The subscript \( n \) is used to number the allowed energy bands (analogous to the Brillouin zones). As \( J_2 \) is small, the energy depends on \( \tau \) almost quadratically. For example, the corresponding dependence for the ground band with \( n = 0 \) reads

\[ E_0(\tau) = \frac{4J_1}{N} \left( 1 - \sqrt{(|\tau| - 1)^2 + \left( \frac{N^2 J_2}{16 J_1} \right)^2} \right)^2 \]

Deviations from the quadratic dependence are most noticeable in the vicinities of integer values of \( \tau \), where narrow energy gaps are formed. The width of the first forbidden band is equal to \( NJ_2 \), the other bands are much narrower. The typical energy spectrum of the Hamiltonian (6) is shown in fig. 2.

Figure 2. The typical energy spectrum (the energy is shown in the units of \( 4J_1/N \)) of the Hamiltonian (6) in the stationary case \( M = 0 \). The splitting of the ground state of dysprosium ions in the crystal field results in the forbidden gaps at the boundaries of the Brillouin-like zones.

A non-stationary electric current \( (M \neq 0) \) induces several nice effects in the dynamics of the toroidal moment. First of all, it is necessary to explore a fairly simple but still important case of adiabatically slow sweeping electric currents, which produce the constant torque \( M << NJ_2 \) (this condition is well satisfied for experimentally achievable values the electric current rates, see numerical estimates in sec. 4). Such a small torque does not noticeably distort the energy spectrum of the Hamiltonian (6) shown in fig. 2. In order to describe the dynamics of the toroidal moment one should consider a wave packet consisting of Bloch functions (7). Under the action of a sweeping current, the wave packet moves along an allowed (Brillouin) zone towards the boundary of the zone, where reflects from it and changes the group velocity of the packet to the
opposite. Then, a new phase of wave-packet acceleration starts, and so on. This process resembles the Bloch oscillations. The evolution of mean values $m$ and $\tau$ are described by equations

$$\frac{d\tau}{dt} = \frac{M}{\hbar}, \quad \frac{d\varphi}{dt} = \frac{1}{\hbar} \frac{dE_n(\tau)}{d\tau}.$$  \hspace{1cm} (8)

During this adiabatic process, the system remains in a state with a definite value of $n$ and the observed physical quantities are oscillating functions in time with Bloch frequency

$$f_0 = \frac{M}{2\hbar} = \frac{T}{8J_1 \frac{4\pi v}{c}},$$  \hspace{1cm} (9)

where $v = dj/dt$ is the constant sweeping rate of the electric current. The oscillations manifest themselves as a series of equidistant steps in the dependence of toroidal moment projection onto the direction of the current (for details, see the next chapter). This quantum effect is essentially a macroscopic quantum coherent effect induced by the swept electric current.

If the external current contains a harmonic component of the frequency $f$ (in addition to the linear term), the Stark-like resonances at frequencies $f = mf_0$ are possible, where $m$ is a rational number.

At higher rates of the current increase there exists a nonzero probability of a tunneling between the ground and the first excited allowed band because of the Zener tunneling. The nature of the effect is that the system penetrates into exited bands through the potential barrier of the energy gaps separating one allowed zone from another. The probability $P_t$ of the tunneling between the ground and the first exited bands per unit time is

$$P_t = f_0 \exp \left( -\frac{\pi}{32} \frac{N^3J_2^2}{M^2} \right).$$  \hspace{1cm} (10)

The Bloch frequency is given by eq. (9).

4. The quantum coherent effects

In this chapter we consider the behavior of the average toroidal moment of a dysprosium cluster under the influence of the planar external electric current. The component of the toroidal moment along the direction of the current is

$$T \cos \theta = \frac{T}{2NJ_1} \left( \frac{4\pi}{c} j(t)T - \frac{N\hbar}{2} \dot{\varphi} \right).$$

As follows from eqs. (8), the sweeping planar current causes the toroidal moment to precess. In the limiting case of free precession ($J_2 = 0$), the average value of the toroidal moment projection on the current direction is zero.

In the case of the Bloch type oscillations ($J_2 \neq 0$), the picture changes drastically. The toroidal moment dependence is the sum of a "normal" linear and a periodic curves with a period $T_{Bl} = 1/f_0$. The toroidal moment experiences characteristic jumps in the magnitude at the moments $t_k = (k - 1/2)T_{Bl}$, $k = 1, 2, \ldots$, or, equivalently, at values $j_k = (k - 1/2)\Delta j$, where $\Delta j$ is the growth of the electric current during one Bloch period. The magnitude of each jump is equal to $\Delta T = 2T_0$. Thus, the graph of the dependence resembles a ladder with steps, which are slightly blurred to the extent that the $J_2$ constant differs from zero.

As mentioned above, the forbidden gaps are a rapidly decreasing with the gap number if $J_2 << J_1$. Therefore, in the first, single-band, approximation it is possible to neglect the Bloch oscillations in the first and the following excited zones. This means that the precession under the influence of the current in all zones, except the ground one, can be considered as free. The
wave packet formed at the initial moment of time, somewhat spreading, reaches the boundary of the Brillouin-like zone, is partially reflected and partially tunnels into the next zone, in which it precesses freely.

The tunneling of the wave packet into the following energy zones makes the magnitude of the magnetization jumps become dependent on the number $k$ of a jump:

$$\Delta T = 2T_0(1 - p)^{k-1},$$

where $p$ is the probability of a tunnel transition from the ground energy band to the first exited band. This probability is the exponential factor present in eq. (10).

![Figure 3. The hopping behavior of the toroidal moment while the electric current sweeps forth and back during three Bloch periods. The interband Zener tunneling results in the hysteresis.](image.png)

In the two-band approximation, one should take into account the Bloch oscillations that occur in the first exited band. Their influence on the shape of the toroidal moment dependence is manifested in the formation of additional jumps that take place strictly midway between the one-band main jumps. The magnitudes of the main and additional jumps are mixed up in view of the possibility of a tunnel transition from the first excited energy band back to the ground band. As a result, the process becomes quite complicated and the formula for the heights of the jumps becomes very bulky.

The described manifestations should reveal on the macroscopic scale, because intermolecular interactions, namely dipole-dipole, which plays a crucial role in the quantum dynamics of SMMs, have been proven experimentally [12] to by negligible for dysprosium based SMT molecules. This means that a whole crystal can be considered as an ensemble of noninteracting dysprosium polygons with strong inter-ions exchange. Therefore the effects considered are macroscopic quantum coherent effects.

In order to provide some numerical we assume that $J_1 \sim 10 \text{ cm}^{-1}$ and $N \sim 10$. Then, at achievable sweeping rates of the electric current up to $10^{13} \text{ A/(cm}^2\cdot\text{s})$, the period $T_{Bl}$ of the Bloch type oscillations is 1 ms. The typical relaxation time (at least 1 ms at helium temperatures [12]) for dysprosium based SMTs allows experimental observation of the effects discussed. The Zener tunneling becomes appreciable ($p \sim 0.05$) if $J_2/J_1 \sim 10^{-5}$, with this, the adiabatic condition of sweeping rates is held.

5. Conclusion

To sum up, a time-dependent electric current induces new exciting coherent quantum effects in the dynamics of a rare-earth single-molecule toroics. These effects include the formation of the band energy spectrum with continuous toroidal quasi-moment states, Bloch-like oscillations, and interband Zener transitions, which are manifested as a hopping increase of the toroidal moment projection onto the electric current direction.

We also believe that the states of such single-molecule toroics near the boundaries of the Brillouin zones can realize a two-level system (qubit), the states of which can be controlled by a time-dependent electrical current.
Finally, despite the fact that we have considered mainly the specific rare-earth dysprosium based single-molecule toroics, many results can be applicable to other Ising-like ions, e.g., Tb$^{3+}$, Ho$^{3+}$, etc.

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