Single magnetic molecule between conducting leads: Effect of mechanical rotations

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Abstract – We study spin-rotation effects in a magnetic molecule bridged between two conducting leads. The dynamics of the total angular momentum couples spin tunneling to the mechanical rotations. The Landau-Zener spin transition produced by the time-dependent magnetic field generates a unique pattern of mechanical oscillations that can be detected by measuring the electronic tunneling current through the molecule.

In the last years a significant experimental effort has been made to measure the electronic current through a single magnetic molecule bridged between conducting leads. These studies have been driven by possible applications of single-molecule magnets in spintronics, as well as by the hope to use magnetic molecules as qubits [1]. Heersche et al. observed a striking voltage dependence of the current through a single-molecule magnet Mn\textsubscript{12}, with a complete current suppression and excitations of negative differential conductance on the energy scale of the anisotropy barrier [2]. Jo et al. measured the magnetic-field dependence of the electron tunneling spectrum in a transistor incorporating a Mn\textsubscript{12} molecule [3]. Henderson et al. observed a Coulomb blockade effect by measuring the conductance through a single-molecule magnet Mn\textsubscript{12} [4]. Voss et al. conducted experiments and developed a theoretical model for the dependence of the tunneling current on the orientation of the Mn\textsubscript{12} molecule [5]. Various aspects of the electronic transport through magnetic molecules have been investigated theoretically. The effect of the exchange coupling between spins of conducting electrons and the spin of the Mn\textsubscript{12} molecule has been studied by G.-H. Kim and T.-S. Kim [6]. Elste and Timm [7] developed a model for the Coulomb blockade in a transport through a single magnetic molecule weakly coupled to magnetic and nonmagnetic leads. They also studied the possibility of writing, storing, and reading spin information in memory devices based upon single-molecule magnets [8]. The Kondo effect in transport through a single-molecule magnet strongly coupled to metallic electrodes has been investigated by Romeike et al. [9]. The effect of spin Berry phase on electron tunneling has been studied by González and Leuenberger [10]. Misiorny et al. investigated magnetic switching of the molecular spin by a spin-polarized current [11], as well as tunneling magnetoresistance [12]. Cornaglia et al. have studied the effect on the transport of a soft vibrating mode of the molecule [13]. First principle DFT calculations of the electron transport through a Mn\textsubscript{12} single-molecule magnet and of the spin-filtering effect have been performed by Barraza-Lopez et al. [14]. There also has been some effort to compute the Josephson current through a magnetic molecule coupled to superconducting leads [15].

Recently two of the authors have demonstrated [16] that quantum states of a magnetic molecule that is free to rotate are different from quantum states of a magnetic molecule whose position is fixed in a crystal. This effect arises from the conservation of the total angular momentum (spin + orbital). A somewhat intermediate situation occurs when a molecule is bridged between two electrodes. While such a molecule is not free to rotate, its orientation can still vary due to the spin-rotation coupling. In this letter we study the Landau-Zener transition between quantum states of the molecule caused by a field sweep. We show that the coupled dynamics of the molecular spin and the mechanical rotation of the molecule leads to the modification of the Landau-Zener dynamics. It also
results in a specific pattern of mechanical oscillations of the molecule. Since electron tunnelling through the molecule should strongly depend on its orientation, this effect should be seen in the tunneling current.

We consider geometry depicted in Fig. 1. The magnetic-anisotropy axis of the molecule, \( Z \), is perpendicular to the direction of the transport current \( Y \). The mechanical motion of the molecule is restricted by its coupling to the leads. For simplicity we consider only small torsional oscillations about the \( Z \)-axis that we describe by the angle of rotation \( \phi \). This is justified by the fact that quantum tunneling of the molecular spin between two opposite directions along the \( Z \)-axis changes only the \( Z \)-component of the angular momentum, thus generating a negligible deformation of a rigid magnetic core of the molecule. On the contrary, the tunneling current through the molecule must have exponential dependence on \( \phi \). We assume that electrons in the leads have only a marginal effect on the quantum spin states of the molecule.

The main part of the Hamiltonian of the molecule has three terms:

\[
\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_Z + \hat{H}_S. \tag{1}
\]

Here

\[
\hat{H}_{\text{rot}} = \frac{1}{2 I_z} \left( \hbar^2 L_z^2 + I_z^2 \omega_\phi^2 \right) \tag{2}
\]
describes mechanical rotations about the \( Z \)-axis. \( I_z \) is the corresponding moment of inertia and \( \omega_\phi \) is the frequency of free torsional oscillations of the molecule due to its coupling to the leads. The operator of the mechanical angular momentum, \( L_z = -i \partial / \partial \phi \), satisfies the commutation relation

\[
[\phi, L_z] = i. \tag{3}
\]

The interaction of the molecular spin \( \mathbf{S} \) with the external magnetic field \( \mathbf{B} \), applied along the \( Z \)-axis, is described by the Zeeman term in eq. (1):

\[
\hat{H}_Z = -g \mu_B S_z B_z, \tag{4}
\]

with \( g \) being the gyromagnetic factor and \( \mu_B \) being the Bohr magneton. The operator \( \hat{H}_S \) in eq. (1) is given by [17,18]

\[
\hat{H}_S = \hat{R} \hat{H}_A \hat{R}^{-1}, \tag{5}
\]

where \( \hat{H}_A \) is the crystal-field (magnetic-anisotropy) spin Hamiltonian and

\[
\hat{R} = e^{-i S_z \phi} \tag{6}
\]

is the operator of rotation in the spin space.

The general form of \( \hat{H}_A \) is

\[
\hat{H}_A = \hat{H}_\parallel + \hat{H}_\perp, \tag{7}
\]

where \( \hat{H}_\parallel \) commutes with \( S_z \) and \( \hat{H}_\perp \) is a perturbation that does not commute with \( S_z \). The existence of the magnetic-anisotropy axis \( Z \) means that the \( | \pm S \rangle \) eigenstates of \( S_z \) are degenerate ground states of \( \hat{H}_\parallel \). The operator \( \hat{H}_\perp \) slightly perturbs the \( | \pm S \rangle \) states, adding small contributions of other \( | m_S \rangle \) states to them. We shall call these degenerate normalized perturbed states \( | \psi_{\pm S} \rangle \). Physically they describe the magnetic moment of the molecule looking in one of the two directions along the anisotropy axis. Full perturbation theory with account of the degeneracy of \( \hat{H}_A \) provides quantum tunneling between the \( | \psi_{\pm S} \rangle \) states. The ground state and the first excited state become

\[
\Psi_{\pm} = \frac{1}{\sqrt{2}} (|\psi_S\rangle \pm |\psi_{-S}\rangle). \tag{8}
\]

They satisfy

\[
\hat{H}_A \Psi_{\pm} = E_{\pm} \Psi_{\pm} \tag{9}
\]

with \( E_- - E_+ = \Delta \) being the tunnel splitting. Expressing \( |\psi_{\pm S}\rangle \) via \( \Psi_{\pm} \) according to eq. (8), it is easy to see from eq. (9) that

\[
\langle \psi_{\pm S} | \hat{H}_A | \psi_{\pm S} \rangle = 0, \quad \langle \psi_{-S} | \hat{H}_A | \psi_S \rangle = -\Delta/2. \tag{10}
\]

This gives

\[
\langle \psi_{\pm S} | \hat{H}_S | \psi_{\pm S} \rangle = 0, \quad \langle \psi_{\mp S} | \hat{H}_S | \psi_{\mp S} \rangle = -\frac{\Delta}{2} e^{\pm 2iS\phi}, \tag{11}
\]

for the matrix elements of \( \hat{H}_S \).

Since the low-energy spin states of the molecule are superpositions of \( | \psi_{\pm S} \rangle \), it is convenient to describe such a two-state system by a pseudospin \( 1/2 \). The components of the corresponding Pauli operator \( \sigma \) are

\[
\sigma_x = |\psi_{-S}\rangle \langle \psi_S | + |\psi_S\rangle \langle \psi_{-S} |, \quad \sigma_y = i |\psi_{-S}\rangle \langle \psi_S | - i |\psi_S\rangle \langle \psi_{-S} |, \quad \sigma_z = |\psi_S\rangle \langle \psi_S | - |\psi_{-S}\rangle \langle \psi_{-S} |. \tag{12}
\]

The projection of any operator \( \hat{H} \) onto \( | \psi_{\pm S} \rangle \) states is given by

\[
\sum_{m,n=\pm S} \langle \psi_m | \hat{H} | \psi_n \rangle \psi_m \langle \psi_n |. \tag{13}
\]
Noticing that
\[ S_z |\psi_{\pm S} \rangle \equiv S_z |\pm S \rangle = \pm S |\psi_{\pm S} \rangle , \]
it is easy to project Hamiltonian (1) onto \( \psi_{\pm S} \). A simple calculation yields
\[ \hat{H}_{\text{eff}} = \hat{H}_{\text{rot}} - \frac{1}{2} W \sigma_z - \frac{1}{2} \Delta \left[ \cos(2S \phi) \sigma_x + \sin(2S \phi) \sigma_y \right] \]
(15)
or
\[ \hat{H}_{\text{eff}} = \hat{H}_{\text{rot}} - \frac{1}{2} \mathbf{H}_{\text{eff}} \cdot \sigma , \]
(16)
where
\[ \mathbf{H}_{\text{eff}} = W e_z + \Delta \cos(2S \phi) e_x + \Delta \sin(2S \phi) e_y \]
(17)
and
\[ W = 2 S g_{\mu B} B_z . \]
(18)

Note that for a nonrotating magnetic molecule the effective Hamiltonian has the form
\[ \hat{H}_{\text{eff}} = - \frac{1}{2} W \sigma_z - \frac{1}{2} \Delta \sigma_z . \]
(19)

Its eigenvalues are
\[ E_{\pm} = \pm \frac{1}{2} \sqrt{W^2 + \Delta^2} \]
(20)
with
\[ E_+ - E_- \equiv \hbar \omega_0 \equiv \sqrt{W^2 + \Delta^2} . \]
(21)

Using the Heisenberg equation of motion for an operator \( A(t) \),
\[ \dot{A}(t) = i \left[ \hat{H}_{\text{eff}}, A(t) \right] , \]
(22)
one obtains
\[ \hbar \dot{L}_z = - I_z \omega_r^2 \phi - S \Delta \left[ \sin(2S \phi) \sigma_x - \cos(2S \phi) \sigma_y \right] , \]
(23)
Elimination of \( L_z \) provides the following system of equations:
\[ \hbar \dot{\sigma}_x = W \sigma_y - \Delta \sin(\phi) \sigma_z , \]
(24)
\[ \hbar \dot{\sigma}_y = \Delta \cos(\phi) \sigma_z - W \sigma_x , \]
(25)
\[ \hbar \dot{\sigma}_z = \Delta \sin(\phi) \sigma_x - \Delta \cos(\phi) \sigma_y , \]
(26)
and
\[ \dot{\varphi} + \omega_r^2 \varphi = \omega_c^2 \left[ \cos(\phi) \sigma_y - \sin(\phi) \sigma_x \right] . \]
(27)

Here
\[ \varphi \equiv 2 S \phi \]
(28)
and
\[ \omega_c \equiv \sqrt{2 S^2 \Delta / I_z } . \]
(29)

Combining the above equations, it is easy to see that they satisfy
\[ \frac{d}{dt} (\hbar L_z + \hbar S \sigma_z ) = - I_z \omega_r^2 \phi . \]
(30)

The left-hand side of this equation is the time derivative of the \( Z \)-component of the total angular momentum, \( \hbar (L_z + S_z) \), while the right-hand side is the elastic torque due to the coupling to the leads (see fig. 1). This torque acts such as to return the molecule to its equilibrium position, \( \phi = 0 \). In the absence of such a torque the total angular momentum of the molecule alone would be conserved.

Equations (24)–(27) are operator equations. To obtain numerically tractable equations, these operator equations should be averaged over the quantum states of the system. If one decouples the quantum averages as
\[ \langle \sin(\varphi) \sigma_z \rangle \Rightarrow \langle \sin(\varphi) \sigma_z \rangle , \]
(31)
in the spirit of the mean-field approximation, one obtains classical-like equations of the same structure as above. Without such a decoupling the equations for the Heisenberg operators are useless and one has to go back to the Schrödinger equation for the whole system consisting of coupled spin and mechanical subsystems. While the decoupling cannot be justified in the general case, we notice that the cross terms containing \( \sigma \) and \( \varphi \) become small when \( \langle \varphi \rangle \) is small. Since \( \varphi = 2 S \phi \) this condition for large \( S \) is stronger than the condition of small oscillations, \( |\varphi| \ll 1 \). Nevertheless, even for \( S = 10 \), which is the case of a Mn12 molecule, it is likely that rotations of the molecule in the geometry depicted in fig. 1 will still satisfy the condition \( |\varphi| \ll 1 \). In this case eqs. (24)–(27) can be treated as classical.

The behavior of the system depends on the dimensionless magneto-mechanical constant of a free molecule,
\[ \delta \equiv \left( \frac{\hbar \omega_c}{\Delta} \right)^2 = \frac{2 \hbar^2 S^2}{I_z \Delta} , \]
(32)
and the resonance parameter,
\[ r \equiv \frac{\hbar \omega_c}{\Delta} , \]
(33)
For a linear field sweep, \( W = v t \), another relevant dimensionless parameter is
\[ \epsilon \equiv \frac{\pi \Delta^2}{2 \hbar v} . \]
(34)
It determines the probability,
\[ P = e^{-\epsilon} , \]
(35)
of staying in the initial \( \psi_{-S} \) state in the standard Landau-Zener problem.

Using the above parameters and dimensionless variables
\[ \tau \equiv \left( \frac{t \Delta}{\hbar} \right) \quad w \equiv \frac{v t}{\Delta} = \frac{\hbar v \tau}{\Delta^2} = \frac{\pi \tau}{2 \epsilon} , \]
(36)
eqs. (24)–(27) for \( |\varphi| \ll 1 \) can be re-written in the form
\[ \sigma'_x = w \sigma_y - \varphi \sigma_z , \]
(37)
\[ \sigma'_y = \sigma_z - w \sigma_x , \]
(38)
\[ \sigma'_z = \varphi \sigma_x - \sigma_y . \]
(39)
and

$$\varphi'' + \gamma \varphi' + r^2 \varphi = \delta [\sigma_y - \varphi_\sigma],$$

where the prime means $\frac{d}{dr}$. Notice that in the last equation we introduced a term $\gamma \varphi'$ that describes the damping of the mechanical oscillations of the molecule.

The above equations have been solved numerically using Mathematica. With the Mn$_{12}$ molecule in mind, we compute the time dependence of the angle of twist, $\phi = \varphi/(2S)$, for $S = 10$, $\delta = 10^3$ and $r = 10^3$ (see discussion below). For the purpose of illustration, the value of the damping constant $\gamma = 0.1$ has been chosen to provide the finite duration of the oscillations. Figure 2 shows the results for a relatively fast field sweep corresponding to $\epsilon = 0.1$. For a slow sweep ($\epsilon \gg 1$) the amplitude of the oscillations is significantly smaller.

Simple arguments allow one to understand the behavior shown in fig. 2. Oscillations of $\phi$ are excited when the time-dependent distance between the spin levels given by eq. (21), coincides with the frequency $\omega_\tau$ of the mechanical oscillations of the molecule. For large $\epsilon \tau$ this happens at $\tau = 2\epsilon \tau/\pi$ in excellent agreement with fig. 2. Oscillations continue at the frequency $\omega_\tau$ until they are completely damped due to the finite $\gamma$. To obtain the dependence of the initial amplitude of the oscillations on the parameters the approximate solution of eqs. (37) for $\sigma_y(\tau)$ at small $\varphi$, $\epsilon < 1$ and $\tau > 1$ can be used [19]:

$$\sigma_y(\tau) = -2 \sqrt{\epsilon e^{-\epsilon}(1 - e^{-\epsilon})} \sin \left( \frac{\pi \tau^2}{4\epsilon} \right).$$

This gives an approximate solution of eq. (38) at $\gamma = 0$:

$$\varphi(\tau) = \frac{\delta}{r} \text{Im} \left[ e^{i\pi \tau} \int_0^\tau \text{d} \tau' e^{-i\tau' \sigma_y(\tau')} \right].$$

The result of the integration can be expressed in terms of trigonometric and error functions. While the formula is rather cumbersome it provides a simple dependence of the final amplitude of the undamped oscillations on the parameters:

$$\phi_{max} = \frac{2hS}{I_s \omega_\tau} \sqrt{\epsilon e^{-\epsilon}(1 - e^{-\epsilon})}. \quad (41)$$

It reaches the maximum at $\epsilon = 1.45$. This expression is in excellent agreement with numerical results. It can be used as long as $2S\phi_{max} \ll 1$.

Most of the existing experiments on transport through individual magnetic molecules have been done with Mn$_{12}$ acetate. The moment of inertia of the Mn$_{12}$ molecule is in the ballpark of $10^{-34}$ g cm$^2$. The tunnel splitting $\Delta$ depends strongly on the transverse anisotropy, $H_\perp$ in eq. (7). For the molecule bridged between two leads it may differ drastically from that in a Mn$_{12}$ crystal. With $I_s \sim 10^{-34}$ g cm$^2$ our choice of $\delta \sim 10^3$ in fig. 2 corresponds to $\Delta/h \sim 10^6$ s$^{-1}$. The resonance frequency of the rotational oscillations of the molecule must be much higher. The choice of $r = 10^3$ in fig. 2 corresponds to $\omega_\tau = 10^6$ s$^{-1}$. The mechanical oscillations of the molecule begin at $t = 2h^2 \omega_\tau/(\pi \Delta^2)$ after the spin states $\psi_{-S}$ and $\psi_S$ cross due to the field sweep. For the choice of parameters used in fig. 2 this time is of order $10^{-4}$ s. The spin oscillations given by eq. (39) must dissipate on a longer time scale for the mechanical oscillations to be observable. In a Mn$_{12}$ crystal, dissipation is dominated by phonons. For a setup shown in fig. 1 phonon processes must be suppressed, making spin relaxation times of order $10^{-4}$ s quite reasonable. For $\Delta/h \sim 10^6$ s$^{-1}$, the fast field sweep, $\epsilon < 1$, corresponds to a few kOe per second, which is also reasonable. Magnetic molecules other than Mn$_{12}$ acetate may prove to be even better candidates for such an experiment.

If a tunneling current flows through the setup depicted in fig. 1, the amplitude of the current should be affected by the mechanical oscillations of the molecule. As in the case of tunneling microscopy, this effect should be detectable due to the high sensitivity of the electron tunneling rate to the orientation of the molecule [5]. Following the field sweep, the current should acquire an oscillating component similar to that shown in fig. 2. Such an experiment is practicable and it would be of great interest as it would probe quantum dynamics of spin in individual magnetic molecules.

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