Magnetic quantum coherence effect in Ni₄ molecular transistors

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Abstract

We present a theoretical study of electron transport in Ni₄ molecular transistors in the presence of Zeeman spin splitting and magnetic quantum coherence (MQC). The Zeeman interaction is extended along the leads which produces gaps in the energy spectrum which allow electron transport with spin polarized along a certain direction. We show that the coherent states in resonance with the spin up or down states in the leads induces an effective coupling between localized spin states and continuum spin states in the single molecule magnet and leads, respectively. We investigate the conductance at zero temperature as a function of the applied bias and magnetic field by means of the Landauer formula, and show that the MQC is responsible for the appearance of resonances. Accordingly, we name them MQC resonances.

Keywords: single molecule magnets, magnetic quantum tunneling, Landauer formula

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

1. Introduction

Single-molecule magnets (SMMs), such as Mn₁₂ [1, 2] and Fe₈ [3, 4], have become the focus of intense research since experiments on bulk samples demonstrated the magnetic quantum tunneling of a single magnetic moment on a macroscopic scale. These molecules are characterized by a large total spin, a large magnetic anisotropy barrier, and anisotropy terms which allow the spin to tunnel through the barrier. It is well known that magnetic quantum coherence (MQC) is realized when the SMM tunnels several times between degenerate spin states with opposite spin projections on the magnetic easy axis before the coherence is destroyed by the environment. Evidence of MQC has been reported for various superconducting systems and for antiferromagnetic nanoclusters [5–10].

Electronic transport through SMMs offers several unique features with potentially large impact on applications such as high-density magnetic storage as well as quantum computing [11, 12]. Recent experiments have pointed out the importance of the interference between spin tunneling paths in molecules. For instance, measurements of the magnetization in bulk Fe₈ have observed oscillations in the tunnel splitting $\Delta_{s,-s}$ between states $S_z = s$ and $-s$ as a function of a transverse magnetic field at temperatures between 0.05 K and 0.7 K (see [13, 14]). This effect can be explained by the interference between Berry phases associated to spin tunneling path of opposite windings [15–19].

In this article we investigate coherent magnetic quantum tunneling in the SMM Ni₄ in which the tunneling rate is faster than the rate of decoherence and at a temperature at which tunneling occurs only between the lowest spin states. We have chosen to study the SMM Ni₄ because of its high symmetry ($S_4$) and large tunnel splittings ($\sim 0.01$ K) at zero magnetic field, which have been confirmed by high frequency EPR and magnetic relaxation experiments [20, 21]. The total spin ground state of Ni₄ is $S = 4$.

The article is organized as follows. First we will start with the model Hamiltonian of the Ni₄ molecular transistor taking into account the magnetic quantum coherence of the two lowest ground spin states of the SMM. Then we will solve this model Hamiltonian and use the solution to calculate the conductance through the molecular transistor as a function of the applied bias by means of the Landauer formalism at zero
temperature for the SMM Ni₂. The conclusions are summarized in the last section.

2. Model Hamiltonian

The total Anderson-type Hamiltonian of a system formed by a single-molecule magnet (SMM) attached to two metallic leads can be separated into three terms

\[ \mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{lead}} + \mathcal{H}_{\text{SMM}} + \mathcal{H}_{\text{SMM-lead}}. \]

We will consider the leads as a one dimensional linear chain of sites. Thus, the first term on the right-hand side of equation (1) is given by

\[ \mathcal{H}_{\text{lead}} = \sum_{\sigma = \uparrow, \downarrow} \sum_{\ell = 1}^{N} \epsilon_{\ell} c_{\ell\sigma}^\dagger c_{\ell\sigma} - V \sum_{\ell \neq \ell'} \left( c_{\ell\uparrow}^\dagger c_{\ell'\downarrow} + c_{\ell\downarrow}^\dagger c_{\ell'\uparrow} \right), \]

where the operator \( c_{\ell\sigma}^\dagger \) (\( c_{\ell\sigma} \)) creates (annihilates) electronic states in the leads with spin orientation \( \sigma = \uparrow, \downarrow \), and energy \( \epsilon_{\ell} \). The symbol \( \langle ij \rangle \) implies the sum over nearest neighbors. The potential of the wire is taken to be zero and the hopping in the wire is \( V \). On the site energies in the leads and in the SMM are given by \( \epsilon_{\ell} = \frac{1}{2} \left[ \epsilon_{\sigma} + \epsilon_{\sigma_0} \right] \) and \( \epsilon_{\sigma_0} \), respectively. \( \Delta_z = \mu_B H_z \) is the Zeeman energy splitting in the leads where \( \sigma_0 \) is the Pauli matrix.

The second term on the right-hand side of equation (1) denotes the SMM part, which can be broken into spin, charging, and gate contributions,

\[ \mathcal{H}_{\text{SMM}} = \mathcal{H}_{\text{spin}}^{(0)} + E_c - q e V_g, \]

where \( E_c \) denotes the charging energy, \( q \) is the number of excess electrons (the charge state of the molecule), and \( V_g \) is the electric potential due to an external gate voltage. In the presence of an external magnetic field, the spin Hamiltonian of the SMM Ni₂ reads

\[ \mathcal{H}_{\text{spin}}^{(0)} = -D_S S_x^2 + C_S (S_y^2 + S_z^2) - \mu_B \gamma H \cdot S, \]

where the easy axis is taken along the \( z \) direction and \( S_x, S_y, S_z \) are the corresponding operators. The magnetic field components were rescaled to \( H_z = \mu_B H / \gamma \) and \( H_{xy} = \mu_B H_z \) for the transversal and longitudinal parts, respectively, where \( g = 2.3 \) denotes the effective gyromagnetic ratio for the giant spin of the SMM and \( D_{\text{quad}} = 0.75 \) K and \( C_{\text{quad}} = 2.9 \times 10^{-4} \) K. The total spin as well as the anisotropy constants \( D_S \) and \( C_S \) depend on the charging state of the molecule, i.e. if the SMM is singly and doubly charged [23]. The longitudinal magnetic field \( H_z \) tilts the double potential well favoring those spin projections aligned with the field. At zero magnetic field the spin projections \( (\uparrow) \) and \( (\downarrow) \) have nearly the same energy and magnetic quantum tunneling is possible. Importantly, for an individual Ni₂ nanomagnet quantum magnetic tunneling is possible only between states that differ by 4 spin units, i.e. if the selection rule \( s_{\uparrow} - s_{\downarrow} = 4 \) is satisfied, where \( k \) is an integer [24]. The transverse magnetic field in the \( xy \) plane lifts the degeneracy of the eigenstates of \( S_y \), by an energy \( \Delta_{xy} \), the so-called tunnel splitting, and leads to states that are coherent superpositions of the eigenstates of \( S_y \). Denoting \( \lambda_{s_{\uparrow} s_{\downarrow}} \) as the coupling matrix element between the states \( | s_{\uparrow} \rangle \) and \( | s_{\downarrow} \rangle \), the magnetic quantum coherence in the single molecule magnet is given by the following effective Hamiltonian

\[ \mathcal{H}_{\text{MQC}} = \lambda_{s_{\uparrow} s_{\downarrow}} (| s_{\uparrow} \rangle \langle s_{\downarrow} | + | s_{\downarrow} \rangle \langle s_{\uparrow} |). \]

where \( \lambda_{s_{\uparrow} s_{\downarrow}} \) represents the source of spin flipping. The most general coherent superpositions for the two lowest levels \( | s_{\uparrow} \rangle, | s_{\downarrow} \rangle \) is given by

\[ |\pm\rangle = \frac{1}{\sqrt{2}} (| s_{\uparrow} \rangle + | s_{\downarrow} \rangle, | s_{\downarrow} \rangle + | s_{\uparrow} \rangle), \]

where

\[ N_\pm = \frac{1}{4} \left( \lambda_{s_{\uparrow} s_{\downarrow}}^2 + \lambda_{s_{\downarrow} s_{\uparrow}}^2 + \lambda_{s_{\uparrow} s_{\uparrow}} + \lambda_{s_{\downarrow} s_{\downarrow}} \right). \]

Note that when \( \lambda_{s_{\uparrow} s_{\downarrow}} \to 0 \) in equation (6) then \( |\pm\rangle \to | s_{\uparrow} \rangle \), which means that there is only one conducting channel open if there is no magnetic quantum coherence.

To take advantage of the coherent superposition in equation (6) we need to singly charge the SMM Ni₂ in order to switch the total spin ground state from \( S = 4 \) to \( S = 9/2 \) or \( S = 7/2 \), the final ground state will be the result of the exchange interaction between the total spins in the SMM. When the nanomagnet is singly charged and with the application of the longitudinal magnetic field \( H_z \) the SMM will only allow electrons with spin down (up) polarization in single electron tunneling transport due to spin blockade. If the SMM has a total spin ground state of \( S = 9/2 \) or \( S = 7/2 \), then there will be transitions from \( | l \rangle \) to \( | l \rangle \) and from \( | l \rangle \) to \( | l \rangle \), respectively. For \( S = 9/2 \) spin up electrons are transmitted through the SMM, whereas for \( S = 7/2 \) spin down electrons are transmitted through the SMM. The energy levels as a function of the orientation of the magnetic moment is pictorially shown in figure 1, where the gap between \( | l \rangle \) and \( | l \rangle \) has been exaggerated to help visualization of the electron transmission through the SMM transistor.

We will be using two pairs of spin ground states \( | s_{\uparrow} \rangle, | s_{\downarrow} \rangle \) and \( | s_{\uparrow} \rangle, | s_{\downarrow} \rangle \) for the uncharged and charged SMM, respectively. For the sake of clarity, we will denote the charged ground states by \( | s_{\uparrow} \rangle \) and \( | s_{\downarrow} \rangle \). With this notation and by restricting the Hilbert space to the lowest spin doublet of the SMM we can then write down the Hamiltonian which represents the interaction of the SMM with the leads

\[ \mathcal{H}_{\text{SMM-lead}} = -t (|\pm\rangle \langle\pm| - |s_{\downarrow} \rangle \langle s_{\uparrow}| - |s_{\uparrow} \rangle \langle s_{\downarrow}|) (|\pm\rangle + |\pm\rangle \langle\pm| - |s_{\downarrow} \rangle \langle s_{\downarrow}| + |s_{\uparrow} \rangle \langle s_{\uparrow}|) (|\pm\rangle + |\pm\rangle \langle\pm| - |s_{\downarrow} \rangle \langle s_{\downarrow}| + |s_{\uparrow} \rangle \langle s_{\uparrow}|). \]

where \( t \) is the lead-molecule tunneling amplitude. Note that the electron tunneling involves either spin up electrons or spin down electrons hopping from the leads into the single molecule magnet (see figure 1). If we substitute equation (6) into the Hamiltonian in equation (8) we obtain the following effective Hamiltonian for the interaction of the SMM with the leads
The stationary state of the total Hamiltonian can be written as \[ |\psi_{s, \pm} = \sum_{j=-\infty}^{\infty} a_{j, \pm}|j\rangle|\pm s\rangle + b_{j, \pm}|0\rangle|\pm s\rangle, \] \( (11) \)

where \( a_{j, \pm}, b_{j, \pm} \) are the probability amplitudes to find the electron at the site \( j \neq 0 \) or at the SMM site \( j = 0 \), respectively, with energy \( \omega = \epsilon_{s, \pm} - 2v \cos(k) \) or \( \omega = \epsilon_{s, \pm} - 2v \cosh(k) \), where \( \epsilon_{s, \pm} = \Delta_{s/2}. \) Substituting equation (11) into the Hamiltonian we obtain the following linear difference equations:

\[ \begin{align*}
\mathcal{H}_{\text{SMM-lead}} &= -\frac{t}{N} \left( \langle -s | c_{11}^{\dagger} + c_{11}^{\dagger}| -s \rangle + \langle -s | c_{11}^{\dagger} + c_{11}^{\dagger}| -s \rangle + \langle -s | c_{11}^{\dagger} + c_{11}^{\dagger}| -s \rangle + \langle -s | c_{11}^{\dagger} + c_{11}^{\dagger}| -s \rangle \right) \\
&= -\Delta_{s, \pm} + \frac{\Delta_{s, \pm}^2 + \Delta_{s, \pm}^2 + \Delta_{s, \pm}^2 + \Delta_{s, \pm}^2}{N}, \end{align*} \]

\( (9) \)

where \( \Delta = \Delta_{s, \pm} - \Delta_{s, \pm} \) and

\[ \begin{align*}
\frac{1}{N} &= \left[ -\frac{\Delta_{s, \pm}}{N} + \frac{\Delta_{s, \pm}^2 + \Delta_{s, \pm}^2 + \Delta_{s, \pm}^2 + \Delta_{s, \pm}^2}{N} \right]. \end{align*} \]

The first term in equation (9) represents a new channel for the electron to tunnel through the molecular transistor which interferes with the direct channel.

The second term represents the electron tunneling from the lead to the SMM with spin-flip processes with tunneling amplitude \( t/N \) and the second term represents the electron tunneling from the lead to the SMM with spin-flip processes with tunneling amplitude \( \Delta. \) Interestingly, if \( \Delta_{s, \pm} \rightarrow 0 \) or \( \lambda_{s, \pm} \rightarrow 0 \) then \( \Lambda \rightarrow 0 \) and there is no spin-flip processes. This shows that magnetic quantum coherence and the coupling between the states \( | \pm s \rangle \) opens a new channel for the electron to tunnel through the molecular transistor which interferes with the direct channel.

### 3. Results

In what follows we present our results for the spin dependent conductance. The stationary state of the total Hamiltonian can be written as \[ |\psi_{s, \pm} = \sum_{j=-\infty}^{\infty} a_{j, \pm}|j\rangle|\pm s\rangle + b_{j, \pm}|0\rangle|\pm s\rangle, \] where \( a_{j, \pm}, b_{j, \pm} \) are the probability amplitudes to find the electron at the site \( j \neq 0 \) or at the SMM site \( j = 0 \), respectively, with energy \( \omega = \epsilon_{s, \pm} - 2v \cos(k) \) or \( \omega = \epsilon_{s, \pm} - 2v \cosh(k) \), where \( \epsilon_{s, \pm} = \Delta_{s/2}. \) Substituting equation (11) into the Hamiltonian we obtain the following linear difference equations:

for \( j \neq -1, 0, 1 \) we have

\[ \begin{align*}
(\omega - \epsilon_{s, \pm}) a_{j, \pm} = -v(a_{j+1, s, \pm} + a_{j-1, s, \pm}), \end{align*} \]

for \( j = -1, 0, 1 \) we have

\[ \begin{align*}
\left( \omega - \epsilon_{s, \pm} \right) a_{-1, s, \pm} &= -v a_{-2, s, \pm} - \frac{t}{N} b_{-s, \pm} - \Delta b_{s, \pm}, \\
\left( \omega - \epsilon_{s, \pm} \right) a_{1, s, \pm} &= -v a_{2, s, \pm} - \frac{t}{N} b_{-s, \pm} - \Delta b_{s, \pm}, \\
\left( \omega - \tilde{\epsilon}_{s, \pm} \right) b_{s, \pm} &= -\frac{t}{N} \left( a_{1, s, \pm} + a_{-1, s, \pm} \right) + \Delta a_{s, \pm} + \Delta a_{-s, \pm}, \end{align*} \]

where \( \tilde{\epsilon}_{s, \pm} = \epsilon_{0, s, \pm} \).

In order to obtain the solution of the above equations we assumed that the spin-up electrons are described by plane waves with unitary incident amplitude coming from the left,
with \( r \) and \( t \) being the reflection and transmission amplitudes, therefore
\[
a_{j\uparrow,-\downarrow} = e^{i\delta_{ij}} + re^{-i\delta_{ij}}, \quad j < 0, \\
a_{j\downarrow,-\uparrow} = e^{i\delta_{ij}}, \quad j > 0, \\
a_{j\downarrow,j\downarrow} = Ae^{i\delta_{ij}}, \quad j < 0 \\
a_{j\uparrow,j\uparrow} = Be^{-i\delta_{ij}}, \quad j > 0.
\] (13)

Substituting equation (13) into equation (12), we get and
\[
\Gamma = \frac{2\sin(k)}{2(i\omega - \bar{\varepsilon}_{01})/N^2 - (\omega - \bar{\varepsilon}_{01})T^2 - 2a^2e^{-x}} \\
+ \Lambda^2 \frac{2\sin(k)}{(\omega - \bar{\varepsilon}_{01}) + 2ae^{ik})(-\omega + \bar{\varepsilon}_{01} + 2ae^{-x})} /N^2
\] (14)

where \( \alpha = \tau' = 2(2 - N^2)/nyN^2. \) If \( \lambda_{\downarrow,-\downarrow} = 0 \) the above equation reduces to a single resonance
\[
\tau = \frac{i\Gamma}{(\omega - e_0) + i\Gamma}
\] (15)

where \( \Gamma = 2\pi \sin(k) \) is the width of the resonance centered at \( \varepsilon_0. \) The conductance for the electron tunneling across the SMM transistor is calculated by means of the Landauer formalism at zero temperature, i.e.
\[
G = \frac{e^2}{h} T(E_F).
\] (16)

where \( e \) is the charge unit, \( h \) is the Planck constant, \( E_F \) is the chemical potential and \( T = |\Gamma|^2. \) The transmission probability at \( \omega = E_F = 0 \) for the spin dependent conductance is
\[
G = \frac{e^2}{h} 4\sin^2(k_F) [\alpha (e_0 + \zeta_+) - \sqrt{(\mu_B gH_F)^2 + \Delta_{s,-s}^2}]^2 \\
\times [2 + \sqrt{(\mu_B gH_F)^2 + \Delta_{s,-s}^2}]^2
\] (17)

where \( \zeta_+ = 2\cosh(k_F), \\zeta_- = 2\tanh^{-1}(\mu_B gH_F) \) and \( \mu_B = \cos^{-1}\left(1 - \frac{\Delta}{4\gamma}\right) \) and \( \zeta_+ = \cosh^{-1}(1 + \Delta/4\gamma). \) In all subsequent calculations we will express energy in temperature units. Therefore, a magnetic field of \( H_z = 1 \text{ T} \) is equal to \( h_B = 1.34 \text{ K} \) and \( 1 \text{ K} \) is equal to a frequency of \( \omega = 1.31 \times 10^{11} \text{ Hz}. \) In what follows we present our results for \( \Delta_s = 0.1 \) and at a fixed longitudinal magnetic field of \( h_B = 0.25 \text{ mK}. \) We used \( \Delta_{s,-s} = 0.005 \text{ K}, \lambda_{\downarrow,-\downarrow} = 0.05 \text{ K} \) and \( N = 1.01 \) for our calculations. The temperature limit to observe this effect would be \( T << 0.01 \text{ K}. \) In figure 2 the spin-dependent conductance versus the gate voltage is depicted for different values of the lead-molecule tunneling amplitude. The conductance shows two resonances as a function of the Fermi energy.

The strong dependence of the conductivity with the tunneling amplitude follows directly from the effective Hamiltonian given in equation (9) in which the electron tunneling with and without spin-flip processes are proportional to the tunneling amplitude. If the lead-molecule tunneling amplitude is weak then a small fraction of the electrons will have

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**Figure 2.** Plots showing the spin-dependent conductance as a function of the gate voltage for different values of the lead-molecule tunneling amplitude. (a) \( t = 5 \text{ K} \) (b) \( t = 6 \text{ K}, \) (c) \( t = 7 \text{ K} \) and (d) \( t = 8 \text{ K}, \) with a constant magnetic field of \( h_B = 0.25 \text{ mK}. \) Note how the MQC effect increases with the coupling interaction.
a spin-flip process and the interference between different tunneling trajectories will not be strong. On the other hand, as the lead-molecule tunneling amplitude increases the interference between different paths is enhanced, therefore, the shift in the peaks is due to the spin-flip processes in the electron transmission. This result shows that the conductance through the SMM transistor depends on the MQC.

4. Conclusions

We have investigated electron transport through a Ni₄ molecular transistor with Zeeman spin splitting and magnetic quantum coherence. We have shown that the transport through the SMM transistor presents a quantum interference between different tunneling trajectories due to the magnetic quantum coherence. Our results are in contrast to the system analyzed in [18] where it is essential to have oppositely spin polarized leads and incoherent spin states in order for quantum interference to take place. These results provide a new method to observe the coherent spin tunneling through MQC resonances of the spin dependent conductance as a function of the gate voltage and of the magnetic field applied in the single molecule magnet.

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