Quantum tunneling induced Kondo effect in single molecular magnets

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We consider transport through a single-molecule magnet strongly coupled to metallic electrodes. We demonstrate that for half-integer spin of the molecule electron- and spin-tunneling cooperate to produce both quantum tunneling of the magnetic moment and a Kondo effect in the linear conductance. The Kondo temperature depends sensitively on the ratio of the transverse and easy-axis anisotropies in a non-monotonic way. The magnetic symmetry of the transverse anisotropy imposes a selection rule on the total spin for the occurrence of the Kondo effect which deviates from the usual even-odd alternation.

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Introduction. Single-molecule magnets (SMMs) such as Mn$_{12}$ or Fe$_8$ have been the focus of intense experimental and theoretical investigation [1]. These molecules are characterized by a large spin ($S > 1/2$), easy-axis and transverse anisotropies, and weak intermolecular interaction. Molecular-crystal properties are due to an ensemble of single molecules and exhibit quantum tunneling of magnetization (QTM) on a mesoscopic scale. Recently, a single molecule magnet (Mn$_{12}$) was trapped in a nanogap [2,3] and fingerprints of the molecular spin were observed in electron transport. Furthermore, transport fingerprints of QTM were predicted [4] when the individual excitations can be resolved by the temperature. Using easy-axis anisotropy for magnetic device operation was also proposed [5]. These works focused on the regime where single electrons charge and discharge the molecule through weak tunneling.

In this Letter we investigate linear transport through a half-integer spin SMM deep inside the blockade regime [6] where the charge on the molecule remains fixed. A strong tunnel-coupling to the metallic electrodes induces spin fluctuations and allows the magnetic moment to tunnel. This is remarkable, since for an isolated SMM with half-integer $S$ this is forbidden by time-reversal (TR) symmetry. At the same time, the resonant spin-scattering allows electrons to pass through the SMM: the Kondo effect for transport [7,8] results in a zero bias conductance anomaly that has been studied experimentally in many systems with small spins (e.g. quantum dots [9,10,11,12,13] and single molecules [14,15]). Such an effect is unexpected in SMMs because the $S > 1/2$ undescreened Kondo effect is suppressed by the easy-axis anisotropy barrier which freezes the spin along the easy axis. However, we find that even a weak transverse anisotropy induces a pseudo-spin-$1/2$ Kondo effect. The corresponding Kondo temperature is experimentally accessible due to a compensation by the large value of the physical spin $S$. We perform a scaling analysis [16] for the effective pseudo-spin-1/2 model and verify the results by a non-perturbative numerical renormalization group (NRG) calculation [17,18] for the full large-spin Hamiltonian.

Model. We consider SMMs which can be described by the following minimal model in the limit of strong tunnel-coupling to electron reservoirs $H = H_M + H_K$:

$$H_M = -DS_z^2 - \frac{1}{2} \sum_{n=1}^{3} B_{2n}(S_{z+}^n(S_{z-}^n) + (S_{z-}^n(S_{z+}^n))$$  

$$H_K = JS \cdot s + \sum_{k\sigma} \epsilon_{k\sigma} a_{k\sigma}^\dagger a_{k\sigma}$$

Here $S_z$ is the projection of the molecule’s spin on the easy axis, chosen as $x$-axis, $S_x = S_z \pm iS_y$, and $s = \sum_{kk'} \sum_{\sigma\sigma'} a_{k\sigma}^\dagger (1/2) \tau_{\sigma\sigma'} a_{k'\sigma'}$. The first term in Eq. 1 describes the easy-axis magnetic anisotropy of the molecule, i.e. the states $|S_z\rangle$, $S_z = -S, \ldots, S$ are its eigenstates. The second term in Eq. 2 describes transverse anisotropy perturbations which in general reduce the symmetry to that of a discrete group of symmetry operations caused by the geometrical structure of the molecule and its ligands via spin-orbit effects. The individual transverse terms written in our model are invariant under 2n-fold rotation $(n = 1, 2, 3)$ about the easy axis. To keep the notation systematic we deviate from the conventional notation for the anisotropies $E = B_2$ and $C = B_4$. Note that the relative strength of the perturbations is $B_{2n} S^{2(n-1)} / D$. The first term in Eq. 2 describes the exchange coupling of the molecular spin to the effective reservoir (the second term in Eq. 2) and thereby transfers charge. The coupling is antiferromagnetic, $J > 0$, in the blockade regime as may be readily shown from the Schrieffer-Wolf transformation [19]. We will show that in a half-integer spin SMM the Kondo effect lifts the blockade of both spin-tunneling (due to TR symmetry) and electron-tunneling (due to energy and charge quantization). Concerning the former effect, for half-integer $S > 1/2$ the eigenstates of the molecular Hamiltonian $H_M$ are at least two-fold degenerate (Kramers doublets) and are linear combinations of states from only one of the disjoint sets $\{ |S \pm (2n)k\rangle \}_{k=0,1,2,\ldots}$, see Fig. 1. Hence the transverse perturbations $B_{2n}$ cannot connect the opposite magnetic basis states $| \pm S\rangle$ as they do for integer spin $S$, i.e. QTM is blocked [20]. However, a Kondo spin-flip process, Eq. 2, can change
$S_z$ by one and connect the disjoint sets of molecular states. Thus in cooperation with the QTM terms the molecular spin can be completely reversed. This is similar to the co-tunneling of nuclear and electronic spins \[21\]. Note that in \[22\] a Kondo effect due to a positive easy-axis anisotropy ($D < 0$) was studied and no transverse anisotropies were considered.

In the following we compare situations where either low- or high-symmetry QTM perturbations dominate. This can be achieved experimentally by a chemical modification of the ligands \[23\] or in transport experiments by changing the binding of the molecule to the electrodes, which can be controlled mechanically in some setups \[24\].

**Poor-man scaling analysis.** To describe the low energy properties of the above model we perform a poor-man scaling analysis \[10\]. This approach leads to similar results as the full NRG calculations (shown in Fig. 2 and discussed at the end), but allows for a detailed discussion of the processes leading to Kondo physics. We truncate the spectrum to the twofold degenerate ground state $|\pm\rangle$ and obtain an effective spin-1/2 Kondo model

$$H_{\text{eff}} = J \sum_{\nu' = \pm} |\nu\rangle\langle\nu'|S|\nu'\rangle s = \sum_{i=x,y,z} j_i s_i,$$  \hspace{1cm} (3)

with the pseudo-spin operators $P_\pm = P_x \pm i P_y = |\pm\rangle\langle\mp|$ and $P_z = (|+\rangle\langle+| - |−\rangle\langle−|)/2$. The effective exchange constants depend on $B_{2n}$, $D$ and $S$ through

$$j_z = 2J|+S_+| > 0,$$  \hspace{1cm} (4)

$$j_{x,y} = J(+|S_+| ± S_-|−)$$ \hspace{1cm} (5)

which we have calculated numerically. Importantly, these constants are completely anisotropic, except for special cases. The scaling equations are $(2W = \text{conduction electron bandwidth}, \rho = \text{density of states})$:

$$\frac{d j_{x,y}}{d \ln W} = -\rho j_s j_y$$ \hspace{1cm} (6)

where $\alpha, \beta, \gamma$ are cyclic permutations of $x, y, z$ \[25\]. Specification of any two scaling invariants $j_{x}^{2} - j_{y}^{2}, \alpha \neq \beta$, defines a 3-dimensional scaling curve. Inversion of any pair of $j_\alpha, j_\beta$ leaves the scaling equations invariant, whereas inverting a single one reverses the flow. Interestingly, all scaling trajectories flow to the strong coupling limit except those in planes of uni-axial symmetry, $|j_\alpha| = |j_\beta| < |j_\gamma|$ with $j_\alpha j_\beta j_\gamma < 0$. In the latter case one has a ferromagnetic fixed line which is unstable with respect to infinitesimal perturbations perpendicular to it which are typically present in our model. If the effective exchange constants lie close to this line the Kondo temperature will thus be strongly suppressed. If the Kondo effect occurs and $|j_z| \geq |j_x| \geq |j_y|$ with $|j_\alpha| \neq |j_\beta|$, we find for the Kondo temperature (defined here as the scale where the first coupling constant diverges)

$$\ln(T_K/W_{\text{eff}}) = -\frac{c_s^{-1} \left( \frac{|j_y|}{\sqrt{j_z^2 - j_y^2}} \frac{j_z^2 - j_{xy}^2}{j_z^2 - j_x^2} \right)}{\rho \sqrt{j_z^2 - j_y^2}}.$$ \hspace{1cm} (7)

Here $c_s^{-1}(u|m)$ is the inverse of the elliptic integral $cs(u|m)$, see \[26\]. In the uni-axial planes $|j_z| = |j_x|$ or $|j_z| = |j_y|$ Eq. (7) reduces to the well-known expressions for easy-axis anisotropy \[27\] since $c_s^{-1}(u|0) = \arctanh(1/u)$ and $c_s^{-1}(u|1) = \arctanh(\sqrt{1 + u^2})$. In this model the upper bound of the Kondo scale $T_K$ is the energy separation between Kramers-degenerate ground and first excited state of the isolated molecule $W_{\text{eff}}(D, \{B_{2n}\})$ which is of the order $0.1 \text{meV} \sim 1 \text{K}$.

According to Eq. (6), the exchange couplings $j_{x,y}$ are generated by spin-tunneling. This gives $j_z > |j_x|, |j_y|$ for not too strong QTM. Thus, the only case where the Kondo effect can not be observed is $|j_z| = |j_y|$ and $j_x j_y < 0$, which using Eq. (6) gives $|+|S_+|−| = 0$. This means that the Kondo effect is not observable when the spin raising operator of the original molecular spin can not flip the pseudo-spin from the down to the up value, an intuitively quite obvious condition. Most importantly, as we will illustrate in the following, this condition can be checked very easily provided the spin and the symmetry of the molecular magnet are given. If a $B_{2n}$ quantum tunneling term is present, we get

$$|+|S_+|−| \neq 0 \Leftrightarrow \frac{2S-1}{2n} = \text{Integer} \hspace{1cm} (8)$$

as a condition for the observability of the Kondo effect in molecular magnets with weak QTM. 

We first consider the limit of a dominant low-symmetry QTM term, $B_{2} \gg B_{4}S_{z}^{2}, B_{6}S_{4}^{4}$. We always find a spin-1/2 Kondo effect, see Fig. 2 because the three couplings are different except for $B_2 = D$. At that point Eq. (11) can be rewritten as $H_{M} = 2DS_{y}^{2} + \text{const}$. The resulting uni-axial symmetric couplings $|j_z| = |j_x| > |j_y|$ allow for a flow to the strong coupling fixed point, also in this case. The Kondo temperature, shown in Fig. 2 has a non-monotonic dependence on $B_{2}/D$, which is enhanced with increasing $S$. For $B_2 \ll D$ (weak QTM), the criterion (8) applies and is always fulfilled for any half-integer spin. The states forming the two ground states $|\pm\rangle$ are connected by the spin raising operator by $S - 1/2$ QTM processes (each contributing a factor $\propto B_2/D$ and one co-tunneling process, see Fig. 1). Therefore, the $B_2/D$ dependence, estimated from Eq. (8), is
The coupling becomes dominant: the Kondo temperature is suppressed again since one decreases with increasing spin. Interestingly, this tendency changes in this regime the Kondo temperature therefore decreases with increasing spin for strong quantum tunneling. Near $B_2 = D$ the perpendicular couplings dominate and grow with increasing $S$: $j_{x,y} = J\sqrt{S(S+1)} + 1/4\) and $j_y = J$ for $B_2 = D$. From Eq. (7) one obtains by expanding in $j_y/j_x \propto 1/S$ an enhancement of $T_K$ with $S \gg 1$:

$$T_K^{B_2=0}/W_{\text{eff}} \propto e^{-\frac{\pi}{J\sqrt{(S+2)+\frac{1}{4}}}}. \quad (9)$$

The exponent becomes $S$-independent for $S \gg 1$. However, the complicated spin-dependent prefactor left out in Eq. (9) decreases with $S$ stronger than $W_{\text{eff}}$ increases: in this regime the Kondo temperature therefore decreases with increasing spin. Interestingly, this tendency changes for larger quantum tunneling. Near $B_2 = D$ the perpendicular couplings dominate and grow with increasing $S$: $j_{x,y} = J\sqrt{S(S+1)} + 1/4\) and $j_y = J$ for $B_2 = D$. From Eq. (7) one obtains by expanding in $j_y/j_x \propto 1/S$ an enhancement of $T_K$ with $S \gg 1$:

$$T_K^{B_2=D}/W_{\text{eff}} \propto e^{-\frac{\pi}{J\sqrt{(S+2)+\frac{1}{4}}}}. \quad (10)$$

In this expression there are two competing factors: increasing $B_2/D$ enhances the r.h.s. of Eq. (10) which is maximal at $B_2 = D$, but simultaneously reduces the splitting $W_{\text{eff}}$ between ground and excited state from $(2S - 1)D$ to $4D$. Hence the maximal Kondo temperature occurs for a value $B_2/D < 1$. Finally, for $B_2 \gg D$ the Kondo temperature is suppressed again since one coupling becomes dominant: $|j_x| \approx J \gg |j_y|, |j_z|$. We note that in the case $B_2 = D$ the molecule can not be considered as a molecular magnet and it is only discussed here to explain the tendency of the increase of the Kondo temperature with increasing spin for strong quantum tunneling. We suggest to study SMMs with moderate quantum tunneling, as e.g. Fe$_{9}$(PPh$_{3}$)$_{18}$ with $D = 0.27$ K and $B_2 = 0.046$ K. For the above mechanism to be relevant the spin $S = 10$ needs to be changed to an half-integer value by changing the charge via a gate electrode. The value of the Kondo exchange coupling depends on the details of the adjacent charge states, e.g. changes in anisotropies and total spin. For a quantitative calculation further input from experiment and ab-initio calculations (e.g. DFT) is needed.

Now we consider a dominant QTM perturbation of higher symmetry, $B_4 \gg B_2/S^2, B_6S^2$. For $B_2 = B_6 = 0$ we have 4 disjoint subsets of basis states which cannot be connected by the QTM term, e.g. for $B_4S^2 \ll D$ the ground states are linear combinations of $\{|S \pm 4k\rangle\}_{k=0,1,2,...}$, see Fig. 3(a,b). While condition $S$ is fulfilled for $S = 5/2 + 2m$, $(m = 0, 1, ...)$, Fig. 3(a), it is violated for $S = 7/2 + 2m$. In the latter case, only the spin lowering operator can increase the pseudospin, Fig. 3(b). However, with increasing $B_4S^2/D$ a level crossing between the ground and excited state of different symmetry results in a sharp change in the Kondo temperature. Hence $B_4$ induces a quantum-phase transition, see Fig. 4 for $S = 7/2$, c.f. 4.

Finally, we mention the possibility that the Kondo coupling can not connect two TR-invariant subsets which leads to a complete vanishing of the effective coupling constants $j_{x,y} = 0$. The lowest order QTM where this effect takes place is of sixth order: in general the Kondo coupling cannot overcome the “mismatch” $|\Delta S_z| = 6$, see Fig. 3(c). In this case only for intermediate or strong $B_6$ a level crossing may give rise to ground states which support a Kondo effect.

**Numerical RG.** We use Wilson’s NRG [17,18] to check the results of our scaling analysis taking into account the full model (i.e. no truncation to a ground state doublet is made). As input parameters we take $J = 0.1W$, number of states $N = 1500$, discretization $\Lambda = 2$ and $D = 5 \times 10^{-3}W$. Since the original procedure has been formulated for a spin-1/2 Kondo model we have modified it to incorporate an arbitrary spin of the impurity.

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**FIG. 2:** Kondo temperature, deduced from the NRG level flow with $J = 0.1W$ and $D = 5 \times 10^{-3}W$, as function of QTM $B_2$ for $S = 3/2, 5/2, 7/2$.

**FIG. 3:** Scheme for the spin selection rule. (a) It is fulfilled for QTM $B_4$ and $S = 5/2$ leading to a Kondo effect. (b) For QTM $B_4$ and $S = 7/2$ the product of the effective couplings $j_{x,y} < 0$ and the Kondo effect is suppressed. (c) For QTM $B_6$ and spin $S = 9/2$. The Kondo coupling can not couple the ground state doublet.

**FIG. 4:** Kondo temperature, deduced from the NRG level flow, as function of QTM $B_4$ for $S = 5/2, 7/2, 9/2$. All other parameters as in Fig. 2.
We analyzed the RG level flow as function of iteration number $N_{\text{iter}}$ in order to determine the low-temperature fixed point and the Kondo temperature which is defined as the energy scale where the crossover to strong coupling takes place. For half-integer spin $S$ and $D > 0$ we observe a flow to the strong coupling fixed point only for a QTM perturbation $B_{2n} \neq 0$, as expected from the above scaling analysis. The Kondo temperature for spin $S = 3/2, 5/2, 7/2$ and dominant $B_2$ QTM is plotted in Fig. 2. It shows in good qualitative agreement with the scaling results the discussed non-monotonic behavior as function of the QTM. For dominant $B_4$ the Kondo temperature is plotted for spin $S = 5/2, 7/2, 9/2$ in Fig. 3. The mapping onto a pseudo-spin-1/2 system is valid as long as there is no crossing of levels and $T_K$ does not exceed the gap to the first excited state. The former is the case for the experimentally most relevant regime $B_{2n} S^{2(n-1)} < D$.

Discussion. Consequently the observation of Kondo-tunneling through SMMs requires a judicious selection of three quantities: (i) the total spin must be half-integer; (ii) the dominant QTM perturbation should be moderate $B_{2n} S^{2n-2} \lesssim D$ and (iii) the total spin should satisfy the selection rule if a high-symmetry QTM term dominates. In experiments where the charge state, and hence the spin state, can be controlled by a gate voltage, the Kondo effect can only be seen in every $(2n)$ subsequent Coulomb diamond for molecules with a dominant $(2n)$ QTM perturbation. This assumes that the spin $S$ increases/decreases by $\frac{1}{2}$ every next charge state and has to be contrasted to the even/odd alternation of the Kondo effect usually observed in quantum dots. It would be of interest to mechanically alter the symmetry of the magnetic core of the SMM in situ, e.g. in a mechanically controlled break-junction setup, and thereby suppress/enhance the Kondo effect.

Summary. Using scaling and numerical renormalization group techniques we have found that spin- and electron-tunneling become correlated in half-integer spin magnetic molecules which are strongly coupled to electrodes. The spin-1/2 Kondo anomaly in the linear conductance signals the externally induced tunneling of the magnetization of the molecule. The Kondo temperature shows a non-monotonic dependence on the relative strength of the transverse magnetic anisotropy of the molecule. Importantly, the large spin of SMMs is found to compensate for anisotropy effects which are expected to suppress Kondo physics. The symmetry of the transverse anisotropy imposes a selection rule: the Kondo effect only occurs for selected values of the molecular spin. We would like to thank K. Kikoin, M. Kiselev, J. Kortus, D. Loss, J. Martinpek, P. Nozières, H. Park, H. van der Zant and A. Zawadowski for discussions. We acknowledge financial support through the EU RTN Spintronics program HPRN-CT-2002-00302 and the FZ Jülich via the virtual institute IFMIT.
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