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 a 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], and fingerprints of the molecular spin were observed in electron transport. Furthermore, transport fingerprints of QTM were predicted [3] when the individual excitations can be resolved by the temperature. Using easy-axis anisotropy for magnetic device operation was also proposed [4]. 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 [5] 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 [6,7] results in a zero bias conductance anomaly that has been studied experimentally in many systems with small spins (e.g., quantum dots [8–12] and single molecules [13,14]). Such an effect is unexpected in SMMs because the $S > 1/2$ *underscreened* 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 [15] for the effective pseudo-spin-1/2 model and verify the results by a nonperturbative numerical renormalization group (NRG) calculation [16,17] 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 $H = H_M + H_K$:

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

$$H_K = J\boldsymbol{S}\cdot\boldsymbol{s} + \sum_{k\sigma}\epsilon_{k\sigma}a_{k\sigma}^\dagger a_{k\sigma}. \tag{2}$$

Here S_z is the projection of the molecule's spin on the easy axis, chosen as the z axis, $S_\pm = S_x \pm iS_y$, and $\boldsymbol{s} = \sum_{kk'}\sum_{\sigma\sigma'} a_{k\sigma}^\dagger(\frac{1}{2}\boldsymbol{\tau})_{\sigma\sigma'}a_{k'\sigma'}$ is the local electron spin in the reservoir ($\boldsymbol{\tau}$ is the Pauli-matrix vector). As usual, the electronic states $|k\sigma\rangle$ are a linear combination of states of both physical electrodes [6,7]. 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. (1) 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-Wolff transformation [18]. 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 twofold degenerate (Kramers doublets) and are linear combinations of states from only one of the disjoint sets $\{|\mp S \pm (2n)k\rangle\}_{k=0,1,2,\ldots}$;

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 [19]. 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 cotunneling of nuclear and electronic spins [20]. Note that in Ref. [21] 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 [22] or in transport experiments by changing the binding of the molecule to the electrodes, which can be controlled mechanically in some setups [23].

Poor-man scaling analysis.—To describe the low energy properties of the above model, we perform a poor-man scaling analysis [15]. This approach leads to similar results as the full NRG calculations (shown in Figs. 2 and 4 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

$$H_{\rm eff} = J \sum_{\nu\nu'=\pm} |\nu\rangle\langle\nu'|\langle\nu|\mathbf{S}|\nu'\rangle \mathbf{s} = \sum_{i=x,y,z} j_i P_i s_i, \tag{3}$$

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

$$j_z = 2J\langle+|S_z|+\rangle > 0, \tag{4}$$

$$j_{x,y} = J\langle+|S_+ \pm S_-|-\rangle, \tag{5}$$

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

$$\frac{dj_\alpha}{d\ln W} = -\rho j_\beta j_\gamma, \tag{6}$$

where α, β, γ are cyclic permutations of x, y, z [24]. Specification of any two scaling invariants $j_\alpha{}^2 - j_\beta{}^2$, $\alpha \neq \beta$, defines a 3-dimensional scaling curve. Inversion of any pair of j_α, j_β 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 uniaxial 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 $|j_z| \neq |j_y|$, we find for the Kondo temperature (defined here as the scale where the first coupling constant diverges)

$$\ln(T_K/W_{\rm eff}) = -\frac{{\rm cs}^{-1}\left(\frac{|j_y|}{\sqrt{j_z^2-j_y^2}} \,\middle|\, \frac{j_z{}^2-j_x{}^2}{j_z{}^2-j_y{}^2}\right)}{\rho\sqrt{j_z{}^2 - j_y{}^2}}. \tag{7}$$

Here ${\rm cs}^{-1}(u|m)$ is the inverse of the elliptic integral ${\rm cs}(u|m)$; see [25]. In the uniaxial planes $|j_z| = |j_x|$ or $|j_x| = |j_y|$, Eq. (7) reduces to the well-known expressions for easy-axis anisotropy [26,27] since ${\rm cs}^{-1}(u|0) = \arctan(1/u)$ and ${\rm cs}^{-1}(u|1) = {\rm arctanh}(\sqrt{1+u^2})$. In this model, the upper bound of the Kondo scale T_K is the energy separation between the Kramers-degenerate ground and first excited states of the isolated molecule $W_{\rm eff}(D, \{B_{2n}\})$, which is of the order 0.1 meV $\sim$ 1 K.

According to Eq. (5), 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 cannot be observed is $|j_x| = |j_y|$ and $j_x j_y < 0$, which using Eq. (5) gives $\langle+|S_+|-\rangle = 0$. This means that the Kondo effect is not observable when the spin raising operator of the original molecular spin cannot flip the pseudospin from the down to the up value, an intuitively quite obvious condition. Most importantly, this condition can be checked very easily, provided the spin and the symmetry of

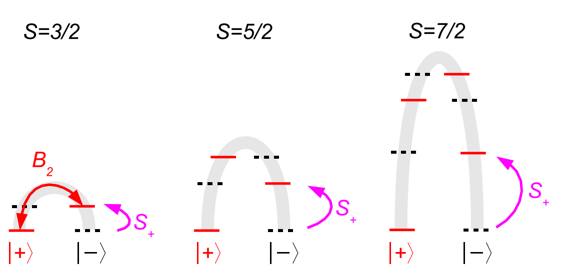

FIG. 1 (color online). Coupling scheme of the ground states including QTM B_2 for $S = 3/2, 5/2, 7/2$. Black (dashed) and red (solid) lines denote $|S_z\rangle$ states belonging to the different TR-invariant subspaces.

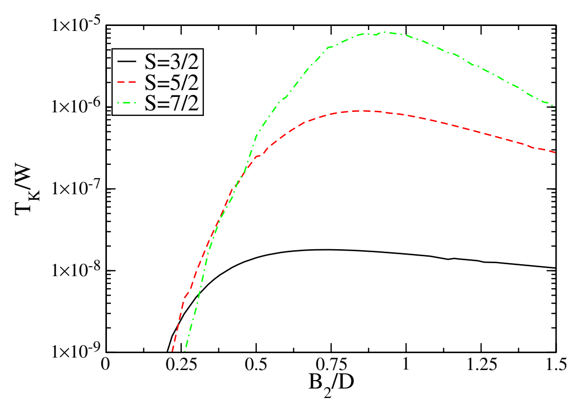

FIG. 2 (color online). Kondo temperature, deduced from the NRG level flow with $J = 0.1W$ and $D = 5 \times 10^{-3}W$, as a function of QTM B_2 for $S = 3/2, 5/2, 7/2$.

the molecular magnet are given. If a B_{2n} quantum tunneling term is present, we get

$$\langle +|S_+|-\rangle \neq 0 \Leftrightarrow \frac{2S-1}{2n} = \text{integer} \tag{8}$$

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, $B_2 \gg B_4 S^2, B_6 S^4$. 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. (1) can be rewritten as $H_{\rm M} = 2DS_y^2 + \text{const}$. The resulting uniaxial 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 nonmonotonic 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 cotunneling process; see Fig. 1. Therefore, the B_2/D dependence, estimated from Eqs. (4) and (5), is $|j_z| \approx 2SJ \gg |j_x| \approx |j_y| \propto (B_2/D)^{S-1/2}$. Using (7), this gives for the Kondo temperature

$$T_K^{B_2 \ll D}/W_{\rm eff} \propto e^{-(1/2\rho J)[1-(1/2S)]\ln(D/B_2)}. \tag{9}$$

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 $W_{\rm eff}$ 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: $j_{x,z} = J\sqrt{S(S+1) + 1/4}$ and $j_y = J$ for $B_2 = D$. From Eq. (7), one obtains by expanding in $j_y/j_z \propto 1/S$ an enhancement of T_K with $S \gg 1$:

$$T_K^{B_2 = D}/W_{\rm eff} \approx e^{-\pi/(2\rho J\sqrt{S(S+1)+1/4})}. \tag{10}$$

In this expression there are two competing factors: Increasing B_2/D enhances the right-hand side of Eq. (7), which is maximal at $B_2 = D$, but simultaneously reduces the splitting $W_{\rm eff}$ between the ground and the 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 cannot 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, such as, e.g., $\text{Fe}_8^{(\text{III})}$ with $D = 0.27$ K and $B_2 = 0.046$ K [28]. For the above mechanism to be relevant, the spin $S = 10$ needs to be changed to a 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., [29]) is needed.

Now we consider a dominant QTM perturbation of higher symmetry, $B_4 \gg B_2/S^2, B_6 S^2$. 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 $B_4 S^2 \ll D$ the ground states are linear combinations of $\{|\mp S \pm 4k\rangle\}_{k=0,1,2,\ldots}$; see Figs. 3(a) and 3(b). While condition (8) is fulfilled for $S = 5/2 + 2m$ ($m = 0, 1, \ldots$) [Fig. 3(a)], it is violated for spin $S = 7/2 + 2m$. In the latter case, only the spin lowering operator can increase the pseudospin [Fig. 3(b)]. However, with increasing $B_4 S^2/D$, a level crossing between the ground and the 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 $S = 7/2$, cf. Ref. [3].

Finally, we mention the possibility that the Kondo coupling cannot connect any two subsets of states, 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 may a level crossing give rise to ground states which support a Kondo effect.

Numerical RG.—We use Wilsons's NRG [16,17] 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. We analyzed the RG level flow as a function of iteration number $N_{\rm iter}$ in order to determine the low-temperature fixed point and the Kondo temperature which is defined

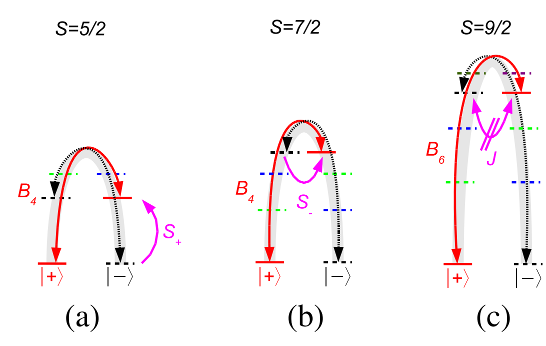

FIG. 3 (color online). Scheme for the spin selection rule. (a) It is fulfilled for QTM B_4 and $S = 5/2$, leading to a Kondo effect. (b) For QTM B_4 and $S = 7/2$, the product of the effective couplings $j_x j_y < 0$ and the Kondo effect is suppressed. (c) For QTM B_6 and spin $S = 9/2$, the Kondo coupling cannot couple the ground-state doublet.

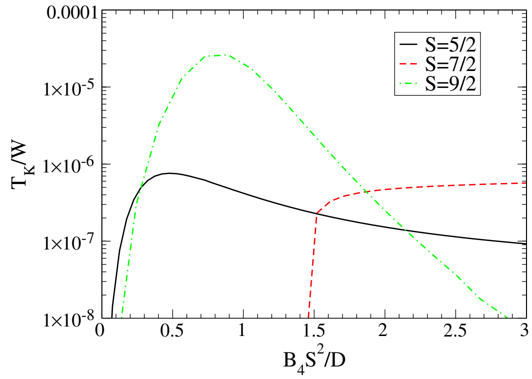

FIG. 4 (color online). Kondo temperature, deduced from the NRG level flow, as a function of QTM B_4 for $S = 5/2, 7/2, 9/2$. All other parameters as in Fig. 2.

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 nonmonotonic behavior as a function of the QTM. For dominant B_4 QTM, the Kondo temperature is plotted for spin $S = 5/2, 7/2, 9/2$ in Fig. 4. 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 a 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 (8) 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 be seen only 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 with 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 [23], and thereby suppress or 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 nonmonotonic 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 occurs only for selected values of the molecular spin.

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