Nonequilibrium excitations in Ferromagnetic Nanoparticles

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In recent measurements of tunneling transport through individual ferromagnetic Co nanograins, Deshmukh, Guérón, Ralph et al.\textsuperscript{1}\textsuperscript{,2} (DGR) observed a tunneling spectrum with discrete resonances, whose spacing was much smaller than what one would expect from naive independent-electron estimates. In a previous publication\textsuperscript{3}, we had suggested that this was a consequence of nonequilibrium excitations, and had proposed a “minimal model” for ferromagnetism in nanograins with a discrete excitation spectrum as a framework for analyzing the experimental data. In the present paper, we provide a detailed analysis of the properties of this model: We delineate which many-body electron states must be considered when constructing the tunneling spectrum, discuss various nonequilibrium scenarios and compare their results with the experimental data of Refs. \textsuperscript{1,2}. We show that a combination of nonequilibrium spin- and single-particle excitations can account for most of the observed features, in particular the abundance of resonances, the resonance spacing and the absence of Zeeman splitting.

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I. INTRODUCTION

An important milestone in the study of itinerant ferromagnetism was reached during the last two years, when Deshmukh, Guérón, Ralph et al.\textsuperscript{1} (DGR) using single-electron tunneling spectroscopy succeeded for the first time to resolve discrete resonances in the tunneling spectrum through individual ferromagnetic single-domain Cobalt nanograins, with diameters between 1 and 4 nm. Their work goes beyond previous studies of ferromagnetic nanograins, in that it seems to be the simplest model possible for a discrete-state system which takes into account the electronic correlations induced by magnetic interactions and which treats the particle’s total spin as a quantum mechanical variable. We argued\textsuperscript{1,2} that the main features of the measured tunneling spectra can be understood within this model by assuming that nonequilibrium spin accumulation occurs, which can produce a much denser spectrum of tunneling excitations than expected within an independent-electron model. The conclusion that nonequilibrium effects play an important role has since been confirmed by more recent measurements by DGR\textsuperscript{2} on a gated device, in which new resonances appeared as the gate voltage was tuned to drive the system further away from equilibrium.

In the present paper, we provide a detailed analysis of equilibrium and nonequilibrium tunneling through ferromagnetic grains, within the framework of our minimal model. The present analysis goes well beyond that of Ref. \textsuperscript{3} in that we consider not only the spin ground states of Fig. 2 in Ref. \textsuperscript{3} but also spin wave excitations and single-particle excitations. The latter turn out to be necessary to understand why a small resonance spacing is observed even when the threshold bias voltage for the onset of tunneling is rather small, so that nonequilibrium effects cannot be very strong.

The structure of the paper is as follows. In Sec. II we summarize the experimental results of Deshmukh et al.\textsuperscript{1} and Guérón et al.\textsuperscript{2}. The Hamiltonian of our minimal model is presented in Sec. III, together with a convenient set of basis states for analyzing the low-lying excitations and their energies. In Sec. IV we discuss two different equilibrium excitations in ferromagnetic grains, namely single particle excitations and spin excitations. A detailed discussion of nonequilibrium excitations and their consequences for tunneling spectra is given in Sec. V.

First we calculate the current through a grain for a nonequilibrium scenario involving only transitions between the ground states \(|s,s\rangle\) of a ladder of spin multiplets of different total spin \(s\); the resonance spacing for
the peaks in the conductance is found to be in quantitative agreement with DGR’s measurements if we assume a total ground state spin of about \( s_0 \sim 1000 \) and that the resonances are predominantly due to the tunneling of minority electrons. We then generalize this nonequilibrium scenario by including also all more highly-excited states \(| s, m \rangle \) of these spin multiplets, finding that if the total spin is large \(( s \gg 1)\), the Zeeman splitting of the observed resonances should be strongly suppressed, in agreement with DGR’s experiments. Finally, we show that a combination of single-particle- and spin excitations in the presence of nonequilibrium can lead to the large number of resonances seen in experiments. Some concluding remarks can be found in Sec. V.

A brief account of our results on the most simple nonequilibrium scenario in ferromagnetic grains has already been given in Ref. 3. The present paper includes a detailed derivation of these results, (Sec. V B), since this paves the way for the more complicated nonequilibrium scenarios presented in Sec. V C and Sec. V D, which have not been reported before.

II. SUMMARY OF EXPERIMENTAL RESULTS

In DGR’s experiments, a nanoscale Cobalt grain was used as a central island in a single electron transistor: it was connected via tunnel barriers to external leads and for one of the grains in Ref. 3 the central grain was also capacitively coupled to a gate. The electronic spectrum of the particle was determined by measuring the tunnel conductance through the grain as function of transport voltage \( V \), [gate voltage \( V_g \)] and magnetic field \( \mu_0 H \) at a fixed temperature of \( T \). The diameters of the Co-grains were estimated as 1-4 nm. Assuming a roughly hemispherical shape, the number of atoms in each grain then is in the range \( N_s \approx 20–1500 \), implying a total spin of \( s_0 \approx 0.83N_s \approx 17–1250 \).

Since the charging energy \(( > 30\text{meV}) \) was very much larger than typical values of the transport voltage \(( eV < 9\text{meV}) \) and the temperature, fluctuations in electron number on the grain are strongly suppressed, so that coherent superposition between different electron numbers \( N \) need not be considered. The energy balance condition that determines through which eigenstates of the grain electrons can tunnel for given values of transport (and gate) voltage thus involve differences between eigenenergies of a grain with fixed particle number \( N \) or \( N \pm 1 \).

\[
\Delta E_{fi}^{\pm} = E_f^{N\pm1} - E_i^{N},
\]

each corresponding to the energy cost of some rate-limiting electron tunneling process \(|i\rangle^N \rightarrow |f\rangle^{N\pm1} \) onto or off the grain. Here \(|i\rangle^N \) denotes a discrete eigenstate, with eigenenergy \( E_i^N \), of a grain with \( N \) electrons, etc. As the magnetic field \( H \) is swept, the resonances undergo energy shifts and crossings.

III. MODEL

In this section we introduce a simple model for ultra-small ferromagnetic grains. The challenge is to describe the individual quantized electronic excitations of a ferromagnetic nanoparticle, taking into account the electronic correlations induced by magnetic interactions and anisotropy forces.
A. Hamiltonian

We propose to model a nanoscale magnet with discrete excitations by the following “minimal” Hamiltonian.\(^{10}\)

\[
\mathcal{H} = \mathcal{H}_C + \mathcal{H}_0 + \mathcal{H}_{\text{exch}} + \mathcal{H}_{\text{Zee}} + \mathcal{H}_{\text{uni}} \quad (2a)
\]

\[
\mathcal{H}_C = eV_D\delta N + E_C\delta \hat{N}^2 \quad (2b)
\]

\[
\mathcal{H}_0 = \sum_{j\sigma} \varepsilon_j c_j^\dagger c_j \quad (2c)
\]

\[
\mathcal{H}_{\text{exch}} = -\frac{U}{2} \mathbf{\hat{S}} \cdot \mathbf{\hat{S}} \quad (2d)
\]

\[
\mathcal{H}_{\text{Zee}} = -\mu H \mathbf{\hat{S}}^z \quad (2e)
\]

\[
\mathcal{H}_{\text{uni}} = -k_N (\mathbf{\hat{S}} \cdot \hat{n})^2/s_0 \quad (2f)
\]

with \(h = g_{\text{eff}}\mu_B\mu_0\mathcal{H} \). Here \(\mathcal{H}_C\) is the standard Coulomb charging energy for a nanoparticle with \(\delta N\) excess electrons. \(V_D = (Q_0 + \sum_j V_j C_j)/C\), for \(r = (L, R, g)\), is the electrostatic potential energy of the island, with \(C \equiv \sum C_r\). \(C_L, C_R\) and \(C_g\) are the tunnel junctions connecting the grain to the left or right lead or the gate electrode, respectively, and \(V_L, V_R\) and \(V_g\) are the voltages of the left/right leads and the gate electrode. \(Q_0\) is an initial random off-set charge and \(E_C = e^2/2C\) is the unit of charging energy.

\(\mathcal{H}_0\) describes the kinetic energy of a single band of single-electron states \(|j, \sigma\rangle\), labeled by a discrete index \(j\) and a spin index \(\sigma = (\uparrow, \downarrow)\), with the spin quantization axis chosen in the \(z\)-direction. The exchange, Zeeman, and anisotropy terms, \(\mathcal{H}_{\text{exch}}, \mathcal{H}_{\text{Zee}}\) and \(\mathcal{H}_{\text{uni}}\), are functions of the total spin vector \(\mathbf{\hat{S}} = \sum_j \hat{S}_j\), where \(\hat{S}_j\) is the spin vector of the electrons in level \(j\).

\[
\hat{S}_j = \frac{1}{2} \sum_{\sigma \sigma'} c_{j \sigma}^\dagger \sigma \sigma' c_{j \sigma'} \quad (3)
\]

(\(\sigma\) are Pauli matrices). \(\mathcal{H}_{\text{exch}}\) is a rotationally invariant term which models the effects of an exchange field and forces the system to adopt a non-zero total ground state spin, say \(s_0\). On account of this term, spins aligned parallel or antiparallel to \((\mathbf{\hat{S}})\) may be thought of as forming “majority” and “minority” bands, which effectively rotate rigidly together with the magnetization direction. We shall take the mean level spacings near the respective Fermi energies, \(d_{\text{min}} \approx 1.19\, \text{eV}/s_0\) and \(d_{\text{maj}} \approx 4.61\, \text{eV}/s_0\), and the exchange-splitting of the Fermi energies, \(\Delta_F \equiv \varepsilon_{F,\text{maj}} - \varepsilon_{F,\text{min}} \approx 2\, \text{eV}\) for \(\mathcal{H}_0\), as characteristic parameters of the model.

\(\mathcal{H}_{\text{Zee}}\) describes the spin Zeeman energy in an external magnetic field \(\mathcal{H} = H \mathbf{\hat{S}}\). Finally, the uniaxial anisotropy \(\mathcal{H}_{\text{uni}}\) is the simplest non-trivial form of an anisotropy modeling the combined effects of crystalline, shape and surface anisotropies, etc. \(\hat{n}\) is the unit vector in the easy-axis direction and \(k_N(>0)\) is a volume-independent constant. \(k_N\) can be estimated from the measured switching field using \(k_N \approx \mu_B H \mathcal{H}_{\text{swc}}\), which yields \(k_N \approx 0.01\, \text{meV}\) [see Ref. 14 in Ref. 3]. For completeness we note that our analysis in a previous paper [Ref. 3] see also Ref. 2] showed that the anisotropy constant \(k_N\) undergoes fluctuations, \(i.e., \) varies between different electronic states within a ferromagnetic nanoparticle. It was shown that these fluctuations have significant consequences for the magnetic field dependence of the resonance energies. However, in the present paper we shall focus only on understanding the characteristic spacings between resonances observed in DGR’s experiments, and not on their magnetic field dependence; we will therefore neglect fluctuations in \(k_N\) throughout this paper.

B. Basis states

Let us for the moment set the anisotropy strength \(k_N = 0\), and use the eigenstates of \(\mathcal{H}(k_N = 0)\) to construct a convenient set of “bare” basis states. Since the Hamiltonian then commutes with the total spin, these states can be grouped into spin multiplets that are labeled by their \(\mathbf{\hat{S}} \cdot \mathbf{\hat{S}}\) and \(\mathbf{\hat{S}}^z\) eigenvalues, say \(s(s+1)\) and \(m\). For example, the bare ground state of \(\mathcal{H}(k_N = 0)\) for given \(N\) and \(h\) \((>0)\), say \(|s, s\rangle_0\), can be written explicitly as a member of the following multiplet of normalized states, \(|s, m\rangle_0\) [illustrated in Fig. 1].

\[
|s, m\rangle_0 = \prod_{j=1}^{n_{\uparrow}} c_{j \uparrow} \prod_{j=1}^{n_{\downarrow}} c_{j \downarrow} |\text{vac}\rangle \quad (4)
\]

\[
|s, m\rangle_0 = \sqrt{(s+m)!/(2s)!} \langle S_- (s-m) |s, m\rangle_0 \quad (5)
\]

Here \(n_{\uparrow, \downarrow} = N/2 \pm s\) and \(S_- = \sum_j c_{j \uparrow}^\dagger c_{j \downarrow}\) is the spin lowering operator. Within this model, the energy difference between the spin multiplet \(|s, m\rangle\) and all other states that are constructed from the same single-electron levels is at least of order \(\varepsilon_{F,\text{maj}} - \varepsilon_{F,\text{min}}\), a very large value \((\approx 2\, \text{eV for Co})\).

The inclusion of a non-zero anisotropy term, \(\mathcal{H}_{\text{uni}}\), will cause the true low-energy eigenstates, \(|s, m\rangle_0\), to be linear superpositions of the bare states in the multiplet \(|s, m\rangle_0\). We choose labels such that \(|s, m\rangle_0 \rightarrow |s, m\rangle_0\) as \(k_N/h \rightarrow 0^+\). We shall call the states \(|s, m\rangle_0\) the spin wave multiplet, since each can be viewed as a homogeneous spin wave.

C. Eigenenergies

In the absence of anisotropies \([\mathcal{H}_{\text{uni}} = 0]\), it is possible to write down explicit expressions for the low-lying excitation energies of our model. Let us denote the excitation energy of a state \(|s, m\rangle_0\) relative to the ground state \(|s_0, m_0\rangle_0\) (for a gated device) by

\[
\delta E(\delta s, \delta m, \delta N) + eV_D \delta N \quad (6)
\]
with $\delta s = s - s_0$, $\delta m = m - m_0$ and $\delta N = N - N_0$. It is straightforward to show that the voltage-independent contribution to Eq. (8) has the following form, first written down by Canali and MacDonald.

\[
\delta E(\delta s, \delta m, \delta N) = (\delta N)^2 \left[ \frac{d_{\text{maj}}}{8} + \frac{d_{\text{min}}}{8} + E_C \right] + \delta N \left[ \varepsilon_F + \frac{d_{\text{maj}}}{4} + \frac{d_{\text{min}}}{4} \right] + \frac{(\delta s)^2}{2} \left[ d_{\text{maj}} + d_{\text{min}} - U \right] + \frac{\Delta_F - U(s_0 + 1/2)}{2} + \delta s \frac{\Delta_N}{2} \left[ \frac{d_{\text{maj}}}{2} - \frac{d_{\text{min}}}{2} \right] - \hbar \delta m.
\]  

(7)

Here we introduced the average of majority- and minority-band Fermi energies $\bar{\varepsilon}_F = (\varepsilon_{F,\text{maj}} + \varepsilon_{F,\text{min}})/2$. The stability of the ground state spin $s_0$, i.e., the requirement that $\delta E(\delta s, \delta m, \delta N) > 0$, implies the relation $\Delta_F = U(s_0 + 1/2) + d_0$, where $d_0(\sim 1/s_0)$ is a small, grain-dependent energy satisfying

$$- (d_{\text{maj}} - U/2) + h < d_0 < d_{\text{min}} - U/2 + h. \quad (8)$$

Hence, the magnitude of $U$ may be estimated as $U \simeq \Delta_F/s_0 \simeq 2eV/s_0$. Note that the ground state spin $s_0$ can be changed by a sufficiently large change in applied magnetic field. However, the range over which the applied magnetic field has to be swept between two successive changes in ground state spin is of order $\delta h \simeq (d_{\text{maj}} + d_{\text{min}} - U)/2$, which is large in nanomagnets ($\mu_0 \delta H \gtrsim 25$ T for Co particles with diameters $\lesssim 4$ nm). Therefore, for a given value of $N$, we shall, as long as we neglect nonequilibrium effects, consider only the “ground state” spin value $s_0$.

### IV. EQUILIBRIUM TRANSITIONS

To construct the tunneling spectrum associated with, say, adding an electron to the grain, we must in principle calculate the excitation energies $\Delta E^{\dagger}_{f,i}$ for all the allowed transitions, i.e., those for which the tunneling matrix element

$$M^\sigma_{fi} \equiv N^{+1} |f| c^\dagger_j \sigma |i\rangle^N \quad (9)$$

is nonzero. For now, we shall neglect nonequilibrium effects and thus consider only those tunneling processes for which the initial state corresponds to the grain’s ground state, i.e. $|i\rangle^N = |s_0, s_0\rangle^N$. In particular, we shall focus on two different types of equilibrium transitions: (A) transitions involving single-particle excitations whose resonance spacing, estimated from the electron density of states, is found to be much larger than observed in DGR’s experiments and (B) transitions between different spin wave states, of which only two transitions are found to have significant weight, leaving unexplained the large number of resonances seen in experiments.

### A. Single particle excitations

Apart from the multiplets $|s, m\rangle^N_0$ discussed in Sec. III B, higher energy multiplets can be built by creating additional single-particle excitations, e.g., by starting from the bare multiplet constructed by applying the spin-lowering operator to the state $c_j^\dagger c_j^\dagger |s, s\rangle^N_0$, with $n_\downarrow < j < n_\uparrow$ and $j' > n_\uparrow$. However, their eigenenergies lie higher than those of the spin wave multiplet $|s, m\rangle^N_0$ by an amount of order $\varepsilon_{j'} - \varepsilon_j$; this is at least of order the single-electron level spacing, $d_{\text{maj}} = 4.61 eV/s_0$ (respectively $d_{\text{min}} = 1.19 eV/s_0$), i.e. rather large compared to $d_{\text{obs}}$ [cf. (P1)]; thus the mechanism causing the observed abundance of low-energy excitations, whatever it is, cannot involve only purely single-particle excitations, but most also involve spin excitations.

### B. Spin wave excitations

We shall now study transitions between two multiplets of spin wave states, with initial states $|i\rangle^N = |s_1, m_1\rangle^N$ and final states $|f\rangle^{N+1} = |s_f, m_f\rangle^{N+1}$. Consider first the large-field regime $h \gg h_{sw}$, where $h_{sw} = g_0 a \mu_B / H_{sw}$. Since here $\mathcal{H}_{\text{zee}}$ dominates over $\mathcal{H}_{\text{anh}}$, we may set $k_N = 0$ and construct the matrix elements $M^\sigma_{fi}$ using the bare spin wave multiplets $|s_1, m_1\rangle^N$ and $|s_f, m_f\rangle^{N+1}$. The condition $M^\sigma_{fi} \neq 0$ then implies the spin selection rules $|s_f - s_i| = 1/2$ and $|m_f - m_i| = 1/2$.

Among all possible final states $|f\rangle$ satisfying these selection rules, Table 1 lists those three which can be reached by adding an electron to the lowest available levels of $|s_0, s_0\rangle^0_0$, namely $j_1 = n_\uparrow + 1$ and $j_2 = n_\downarrow + 1$: A spin$^\uparrow$-electron can be added only to level $j_1$ (Table 1 column 1), whereas a spin$^\downarrow$-electron can be added to either level $j_1$ (row 2) or $j_2$ (row 3).

The excitation energies $\Delta E^\dagger_{f,i}$ (Table 1 column 4) of the $(j_1 \uparrow)$ and $(j_2 \downarrow)$ transitions are degenerate at $h = 0$ and Zeeman-split as a function of $h$, but, in accord with (P3), this splitting will not be observable: the weight of the $(j_1 \downarrow)$ transition is smaller than that of the $(j_1 \uparrow)$ transition (Table 1 column 3) by a Clebsch-Gordan coefficient of order $1/(2s_0)$ which is negligibly small for
large-\(s_0\) grains. The \((j_1 \uparrow)\) and \((j_2 \downarrow)\) transitions both have large, comparable weights, and would produce resonances with large-\(h\) slopes of opposite signs. Depending on whether the difference in their excitation energies \(E_{s_0} + \varepsilon_{\text{maj}} + d_{\text{maj}} - (U/2)(s_0 + 3/4) - h/2\) is close to or far from 0 (it is at most of order \(d_{\text{maj}}\) - \(U/2\), i.e. \(\lesssim 3\text{meV}\) for a 4-nm -diameter Co particle), either both or only one of the \((j_1 \uparrow)\) and \((j_2 \downarrow)\) transitions would be observable in the regime of lowest excitation energies (say \(\lesssim 0.5\text{meV}\)). In an equilibrium transition scenario, this leaves unexplained the large observed density of tunneling resonances (P1), since, apart from these two transitions, there are no others with significant weight and excitation energies less than \(d_{\text{maj}}\) (\(d_{\text{min}}\)).

Next we argue that this problem persists also for the case with anisotropy, where \(k_N \neq 0\). A priori one might have expected to see more low-lying excitations then, since, apart from these two transitions, there are no others with significant weight and excitation energies less than \(d_{\text{maj}}\) (\(d_{\text{min}}\)).

Thus, even though \(H_{\text{uni}}\) causes violations of one of the spin selection rules, the extra transitions have too little weight to explain the large density of low-energy excitations that is observed (P1). The \((j_1 \uparrow)\) and \((j_2 \downarrow)\) transitions both have large, comparable weights, and would produce resonances with large-\(h\) slopes of opposite signs. Depending on whether the difference in their excitation energies \(E_{s_0} + \varepsilon_{\text{maj}} + d_{\text{maj}} - (U/2)(s_0 + 3/4) - h/2\) is close to or far from 0 (it is at most of order \(d_{\text{maj}}\) - \(U/2\), i.e. \(\lesssim 3\text{meV}\) for a 4-nm -diameter Co particle), either both or only one of the \((j_1 \uparrow)\) and \((j_2 \downarrow)\) transitions would be observable in the regime of lowest excitation energies (say \(\lesssim 0.5\text{meV}\)). In an equilibrium transition scenario, this leaves unexplained the large observed density of tunneling resonances (P1), since, apart from these two transitions, there are no others with significant weight and excitation energies less than \(d_{\text{maj}}\) (\(d_{\text{min}}\)).

We therefore assert that the large density of resonances cannot be explained by equilibrium transitions alone; we will explore nonequilibrium effects below.

V. NONEQUILIBRIUM TRANSITIONS

Since the large density of resonances (P1) cannot be explained by equilibrium transitions (neither single-particle excitations (Sec. IV A) nor spin wave excitations (Sec. IV B)), we shall in this section explore nonequilibrium effects. Our conclusion will be that a combination of nonequilibrium spin and single-particle excitations produces a much denser spectrum of tunneling states than expected within an independent-electron model. For a spin of \(s_0 \approx 1000\), this nonequilibrium scenario gives a resonance spacing of \(\approx 0.2\text{meV}\) for the spacing of resonances due to the tunneling of minority electrons, in accord with the observed resonance spacing.

Nonequilibrium spin accumulation had of course already been studied previously in the context of single-electron transistors with ferromagnetic components, and spin accumulation for nanograins with discrete energy levels was first analysed by Barnás et al. However, these analyses all employed a single-particle description in which all states that were considered were simple
Slater determinants of single-particle states. Within our present model, we have to go beyond this simple picture by considering the true many-body eigenstates of the Hamiltonian, which are in general linear combinations of Slater determinants.

After explaining the general idea of nonequilibrium processes in ferromagnetic grains in Sec. V A, we shall describe different nonequilibrium scenarios. For each, we calculate the corresponding theoretical tunnel spectra and compare resonance spacings and the number of resonances with DGR’s measurements. We show in Sec. V B and compare resonance spacings and the number of resonances.

For each, we shall describe different nonequilibrium scenarios. For each, we calculate the corresponding theoretical tunnel spectra and compare resonance spacings and the number of resonances with DGR’s measurements. We show in Sec. V B and compare resonance spacings and the number of resonances.

A simple scenario is illustrated in Fig. 3. Even if a first tunneling event causes a “charging” transition from the N-electron ground state $|\gamma_0\rangle^N$ to the $(N \pm 1)$-electron ground state $|\gamma_{N\pm 1}\rangle^N$, it may be energetically possible for the subsequent “discharging” tunneling transition to return the particle to an excited N-electron state $|\gamma_e\rangle^N$ instead of $|\gamma_g\rangle^N$, provided the applied voltage is sufficiently large, $eV \gtrsim E_e^N - E_g^N$. Likewise, further charging and discharging transitions may allow any of a large ensemble of states to be occupied at higher and higher levels of an energy ladder, terminating only when an energy-increasing transition requires more energy than the applied voltage provides. As the voltage is increased, the total current (or conductance) may increase stepwise (or show peaks) when thresholds are crossed to allow higher-energy transitions up the nonequilibrium ladder, thereby changing the occupation probabilities of the ensemble of nonequilibrium states and opening new tunneling channels.

Let $\{\gamma\}$ be the set of all states involved in a nonequilibrium ladder of excitations, i.e., the set of all discrete states with a nonzero occupation probability $P(\gamma)$ for a given bias voltage, gate voltage, temperature and magnetic field. To find the occupation probability $P(\gamma)$ for all the states $|\gamma\rangle$ of the ladder one has to solve a normalization condition $\sum \gamma P(\gamma') = 1$ and a stationary master equation of the form

$$0 = \sum_{\gamma' \neq \gamma} \left\{ \Sigma_{\gamma\gamma'} P(\gamma') - \Sigma_{\gamma'\gamma} P(\gamma) \right\}$$

for each $\gamma$. The first (second) term in Eq. (10) describes the rate at which the probability of a given configuration increases (decreases) due to electrons tunneling onto or off the grain, the remaining terms are associated with electronic relaxation and spin-flip relaxation on the grain, respectively.

$\Sigma_{\gamma\gamma'}$ is the total tunneling-induced transition rate from initial state $|\gamma'\rangle$ to final state $|\gamma\rangle$. Considering sequential tunneling only, it has the form

$$\Sigma_{\gamma\gamma'} = \sum_{r=1}^{N} \sum_{p=\pm} \Sigma_{\gamma\gamma'}^{r}$$

where $\Sigma_{\gamma\gamma'}^{r}$ (or $\Sigma_{\gamma\gamma'}^{r-}$) involves the coherent transfer of an electron onto (from) the grain from (onto) the lead $r$ and is given by

$$\Sigma_{\gamma\gamma'}^{r} = \Gamma_r \sum_{i\sigma} |\langle \gamma^0 | c_{i\sigma}^\dagger | \gamma^r \rangle|^2 f(E_r - E_{\gamma} - eV_r)$$

and

$$\Sigma_{\gamma\gamma'}^{r-} = \Gamma_r \sum_{i\sigma} |\langle \gamma^0 | c_{i\sigma}^\dagger | \gamma^r \rangle|^2 f(E_r - E_{\gamma} + eV_r).$$

Here $f(E) = 1/(e^{E/k_BT} + 1)$ is the Fermi function and $eV_r$ is the electrostatic potential energy difference between lead $r$ and the grain,

$$eV_r \equiv eV_r - eV_D.$$
The third and fourth terms in Eq. (10) describe electronic (spin-conserving) relaxation processes inside the grain. For simplicity, we shall only consider electronic relaxation between energetically “neighboring” single particle levels, i.e. we take

$$\Sigma_{\gamma'\gamma}^\pm = \Gamma_1 \sum_{\sigma} \left| \langle \gamma' | e^{i(i-1)\alpha} C_{\sigma} | \gamma \rangle \right|^2.$$  \hspace{1cm} (13)

(Generalizations of this assumption are straightforward, though cumbersome.) The last two terms of Eq. (10) describe the rate at which the probability of a given distribution increases (decreases) due to spin-flip relaxation in the ferromagnetic grain. For simplicity we shall assume all spin-flip relaxation rates to be much smaller than all other rates, $\Gamma_{\text{sf}} < \Gamma_{\text{tun}}$, and hence take $\Sigma_{\gamma'\gamma}^\pm = 0$ throughout this paper.) (Again, it is straightforward to consider generalizations of this case.) Moreover, all rates $\Gamma$ are assumed to be independent of the specific single particle level $\sigma$ involved.

The current through the grain can then be calculated as

$$I_r = e \sum_{\gamma'} \left( \Sigma_{\gamma'\gamma}^+ - \Sigma_{\gamma'\gamma}^- \right) P(\gamma').$$ \hspace{1cm} (14)

B. Spin accumulation

In a ferromagnetic particle, in addition to the nonequilibrium occupation of single-electron states discussed previously for non-magnetic particles, nonequilibrium spin excitations are possible, too, if the spin-flip rate $\Gamma_{\text{sf}}$ is smaller than the tunneling rate $\Gamma_{\text{tun}}$. In this case a ladder of transitions will occur between states with different total spin $s$, causing each to have a finite occupation probability and thus leading to spin accumulation on the grain.

The simplest nontrivial case, namely a ladder of spin multiplet ground states $|s, s\rangle$ (see Fig. 3) was already briefly discussed in Ref. 3. Below we shall discuss this case in more detail. We shall calculate the resonance spacing of steps in the current (or of peaks in the distribution) and the number of resonances for transitions between spin ground states. We shall characterize spin ground states by their spin and charge relative to the overground state, i.e. we shall write

$$||\delta s; \delta N|| \equiv |s_0 + \delta s, s_0 + \delta s\rangle_{N_0 + \delta N},$$ \hspace{1cm} (15)

with $\delta s$ and $\delta N$ as defined in Sec. IIC after Eq. 4. We shall find that the resonance spacing agrees very well with DGR’s measurements.

Consider a sequence of nonequilibrium transitions forming a “ladder” ($L_{n,1}^{\alpha}$) with “run index” $n = 0, 1, 2, \ldots$, where each run corresponds to a “charging” transition ($L_{n,1}^{\alpha}$) followed by a “discharging” transition ($L_{n,2}^{\alpha}$):

$$||\alpha p n; 0|| \xrightarrow{L_{n,1}^{\alpha}} ||\alpha p (n + 1/2); p|| \xrightarrow{L_{n,2}^{\alpha}} ||\alpha p (n + 1); 0||.$$  \hspace{1cm} (16)

(Above, the notation $||\delta s; \delta N||$ is used.) The indices $p$ and $\alpha$ are used to distinguish whether the first electron that tunnels enters or leaves the grain, $p = (+1, -1)$, and whether it is a majority or minority electron, $\alpha = (\text{maj}, \text{min}) = (+1, -1)$.

Using Eq. (10), the threshold energy costs for transitions $L_{n,1}^{\alpha}$ and $L_{n,1}^{\alpha}$ can be calculated to be

$$\Delta E_{n,1}^{\alpha} = E(\alpha p (n + 1/2); p) - E(\alpha p; 0)$$  \hspace{1cm} (16a)

$$= \Delta E_{0,1}^{\alpha} + n [d_a - U/2],$$

$$\Delta E_{n,2}^{\alpha} = E(\alpha p (n + 1); 0) - E(\alpha p (n + 1/2); p)$$  \hspace{1cm} (16b)

$$= \Delta E_{0,2}^{\alpha} + n [d_a - U/2],$$

with

$$\Delta E_{0,1}^{\alpha} = d_a (1 + p)/2 + E_C + p(\xi_F + \alpha d_0)/2 - U/8,$$

$$\Delta E_{0,2}^{\alpha} = d_a (1 - p)/2 - E_C - p(\xi_F - \alpha d_0)/2 - 3U/8.$$  \hspace{1cm} (17)

Note that the total energy cost for the combined transitions $L_{n,1}^{\alpha}$ and $L_{n,1}^{\alpha}$, namely

$$\Delta E_{0,1}^{\alpha} = \Delta E_{0,1}^{\alpha} + \Delta E_{0,2}^{\alpha}$$  \hspace{1cm} (17a)

$$= d_a \frac{1 + p}{2} + d_a \frac{1 - p}{2} + p a d_0 - \frac{U}{2},$$ \hspace{1cm} (17b)

is always $\geq 0$; this follows intuitively from the fact that $\Delta E_{0,1}^{\alpha}$ is the excitation energy between the overall ground state $||\delta s; \delta N|| = ||0; 0||$ and the adjacent-spin ground state $||\alpha p; 0||$, and more formally from condition 6 on $d_0$.

Assuming that the peaks in the conductance are due to successive charging transitions becoming accessible as the bias voltage is increased, the resonance spacing for the ladder $L_{n}^{\alpha}$ can readily be calculated using Eqs. (16):

$$\delta E_{\text{res}}^{\alpha} = \Delta E_{n+1,1}^{\alpha} - \Delta E_{n,1}^{\alpha}$$  \hspace{1cm} (18a)

$$= d_a - U/2.$$ \hspace{1cm} (18b)

This result, which evidently depends only on whether the charging transition involves the tunneling of a majority or minority electron, $\alpha = (\text{maj}, \text{min})$, can be intuitively understood as follows: The resonance spacing, $\delta E_{\text{res}}^{\alpha}$, is a difference of energy differences, i.e. a type of (discrete) second derivative of the total energy. The contribution $d_a$ reflects the discrete second derivative w.r.t. the quasiparticle number of the energy involved in creating, using only $\alpha$-electrons, $n$ particle-like or hole-like excitations relative to the overall ground state, and the term $-U/2$ reflects the discrete second derivative w.r.t. the spin of the exchange energy. The partial cancellation between $d_a$ and $-U/2$ in Eq. (18b) reflects the opposite signs of the kinetic and exchange energies in the Hamiltonian (4), and is thus very generic. Very significantly, since $U/2$ and $d_{\text{min}}$ (but not $d_{\text{maj}}$) happen to be almost equal, this partial cancellation of two rather large energies produces a
much smaller energy,
\[
\Delta E_{\text{res}}^{\text{min},p} \approx (1.2 - 1.0)eV/s_0 = 0.2 \ eV/s_0 ,
\]
where we used the parameter estimates given in Secs. II and III. This brings us to one of the main conclusions of this paper: the small resonance spacing of 0.2 meV observed by DGR is consistent with prediction (19) for minority-electron charging events if the ground state spin is assumed to be about s_0 \approx 1000, which is within the estimated size range of DGR's grains. Satisfactorily, the conclusion that minority electrons dominate the charging transitions, which was reached independently by Canali and MacDonald too [2], has recently been confirmed experimentally for DRG's gated device, as has been the conclusion that nonequilibrium physics is involved [cf. points (P4) and (P5) of Sec. II].

We shall therefore henceforth consider only the case that charging transitions are due to minority electrons, i.e., we take \( \alpha = \min \) (but for notational brevity will sometimes still use the index instead of \( \alpha \)). The conductance will then show a limited number, say \( n_{\text{res}}^{\text{ch}} \), of resonances due to charging transitions, with a rather small spacing of \( d_{\text{min}} - U/2 \), followed by an unlimited number of resonances due to discharging transitions, with a much larger spacing of \( d_{\text{maj}} - U/2 \). This can be seen as follows: let us consider for definiteness a circuit with \( V_L = -V_R = V/2 \), and suppose that \( eV > 0 \), so that electrons flow from left to right through the ferromagnetic grain. Then transition \( L_{\text{res}}^{\text{op},1} \) involves tunneling across the left junction if \( p = 1 \), or the right junction if \( p = -1 \), and likewise \( L_{\text{res}}^{\text{op},2} \) involves tunneling across junction \((R,L)\) for \( \bar{p} = (-1,1) \). The voltage thresholds, say \( eV_{\text{res}}^{\text{op},1} \) (or \( eV_{\text{res}}^{\text{op},2} \)), needed to overcome the energy cost \( \Delta E_{\text{res}}^{\text{op},1} \) (or \( \Delta E_{\text{res}}^{\text{op},2} \)) in order for the charging transition \( L_{\text{res}}^{\text{op},1} \) (or the discharging transition \( L_{\text{res}}^{\text{op},2} \)) to occur, are determined by the conditions:
\[
peV_p \geq \Delta E_{\text{res}}^{\text{op},1},
\]
\[
\bar{p}eV_p \geq \Delta E_{\text{res}}^{\text{op},2}.
\]
Here \( eV_p \), the electrostatic potential energy difference between lead \( p \) and the grain, is [from Eq. (22)] related to the actual applied voltage by
\[
eV_p = eVB_p - eV_\delta,
\]
where \( B_p \equiv (C_p + C_g/2)/C \) is a capacitance ratio which converts applied voltage to energy, and \( eV_\delta \equiv e(Q_0 + V_\delta C_g)/C \) is an offset energy. It follows from Eqs. (21) and (22) that \( V_{\text{res}}^{\text{op},1} \) and \( V_{\text{res}}^{\text{op},2} \) are given by
\[
B_p eV_{\text{res}}^{\text{op},1} = \Delta E_{\text{res}}^{\text{op},1} + peV_\delta,
\]
\[
B_\bar{p} eV_{\text{res}}^{\text{op},2} = \Delta E_{\text{res}}^{\text{op},2} - peV_\delta.
\]
In particular, the threshold voltage \( V_{\text{res}}^{\text{op},1} \) for the first charging transition, \( L_{\text{res}}^{\text{op},1} \), determines the measured size of the Coulomb-blockade region (in energy units), say \( E_{\text{C}}^{\text{thresh}} \):
\[
E_{\text{C}}^{\text{thresh}} \equiv eV_{\text{res}}^{\text{op},1}B_p = \Delta E_{\text{res}}^{\text{op},1} + peV_\delta.
\]
This enables us to eliminate \( peV_\delta \) from Eq. (22) and write it as [using Eqs. (10) and (17a)]
\[
B_p eV_{\text{res}}^{\text{op},1} = n(d_\alpha - U/2) + E_{\text{C}}^{\text{thresh}},
\]
\[
B_\bar{p} eV_{\text{res}}^{\text{op},2} = n(d_\alpha - U/2) - E_{\text{C}}^{\text{thresh}} + \Delta E_{\text{res}}^{\text{op},p}.
\]
Now, whenever \( E_{\text{C}}^{\text{thresh}} \geq \frac{1}{2}\Delta E_{\text{res}}^{\text{op},p} \), i.e., whenever \( E_{\text{C}}^{\text{thresh}} \) is not too small, the inequality
\[
eV_{\text{res}}^{\text{op},1} > \frac{1}{2}\Delta E_{\text{res}}^{\text{op},p},
\]
will hold for sufficiently small values of \( n \) (at least for \( n = 0 \)). However, for large enough \( n \) it will cease to hold, since for the case \( \alpha = \min \) that we are considering, the “step size” \( d_{\text{maj}} - U/2 \) for \( eV_{\text{res}}^{\text{op},1} \) is much larger than the “step size” \( d_{\text{min}} - U/2 \) for \( eV_{\text{res}}^{\text{op},2} \). Thus, the first few measured conductance resonances will be due to a sequence of (rather closely-spaced) charging transitions, as opposed to (much more widely-spaced) discharging transitions, because each time the bias voltage is incremented by \( eV_{\text{res}}^{\text{op},1} \) to make the next charging transition \( L_{\text{res}}^{\text{op},1} \) energetically accessible, this bias voltage increment is already large enough (namely \( > eV_{\text{res}}^{\text{op},2} \)) to also allow the discharging transition \( L_{\text{res}}^{\text{op},2} \) to occur. However, once the inequality

![FIG. 4: Current as function of eVBL for the following parameters: α = min, p = +1, s_0 = 10, d_\min = 1.19 eV/s_0, d_\maj = 4.61 eV/s_0, U = 2 eV/s_0, B_L = 0.3, B_R = 0.7, E_{\text{C}}^{\text{thresh}} = 0.8 eV/s_0, E_{\text{G}}^{\text{op},1} = 0 eV/s_0, \Gamma^f/\Gamma^R = 0.8, \Gamma_\alpha = 0, T = 80 \text{ mK} \]
Eq. [25] is violated, the subsequent discharging transition $E_{n,2}^{ch}$ will become possible only after the total bias voltage increment reaches $eV_{\alpha p}^{ch}$, i.e., henceforth discharging (instead of charging) transitions will determine the conductance resonances, which will henceforth be spaced much more widely.

To calculate the total number of closely-spaced resonances due to charging transitions, $n_{\text{res}}^{\text{ch}}$, we must thus determine how large $n$ can become before the condition Eq. (24) ceases to hold. Using Eqs. (24) and $B_p+B_d=1$, this condition can be rearranged to yield an expression for $n_{\text{res}}^{\text{ch}}$, which is found to be given by the smallest integer larger or equal to

$$1 + \frac{E_{\text{C}}^{\text{thresh}} - B_p\Delta E_{0,\text{tot}}}{B_p(d_{\text{max}} - U/2) - B_p(d_{\text{min}} - U/2)}.$$  \hspace{1cm} (26)

The prediction that $n_{\text{res}}^{\text{ch}}$ increases linearly with $E_{\text{C}}^{\text{thresh}}$ is in qualitative agreement with Fig. 2 of Ref. [8]. However, it is not entirely consistent with more recent data on Co-grains [8] where, even when the Coulomb blockade threshold was very small ($E_{\text{C}}^{\text{thresh}} \lesssim 1$ meV), the differential conductance showed many (>10) peaks, i.e., many more than Eq. (24) would predict. To illustrate this, we have solved Eq. (11) numerically for the discussed transitions and calculated the current for the parameters of the model and a threshold charging energy of $E_{\text{C}}^{\text{thresh}} = 0.8 \text{eV}/s_0$ as function of $eVB_L$ [see Fig. 3(a)]. The calculated current shows three steps in the plotted region. Experimental data (see Fig. 1 in Ref. 3) on the other hand show $\approx 12$ resonances for the parameters used.

To summarize the conclusions of this section: a nonequilibrium scenario involving only spin ground states, and assuming charging transitions involving minority electrons, results in a spacing of resonances, $\delta E_{\text{res}} \approx 0.2 \text{meV}$ for $s_0 = 1000$, that agrees roughly with the spacing observed. However, the number of resonances predicted by Eq. (21) is sometimes much smaller than observed, namely when $E_{\text{C}}^{\text{thresh}}$ is small (on the order of $d_{\text{min}}$).

**C. Spin wave excitation**

In the preceding section, we considered only transitions between different spin ground states, $|s, s\rangle$; we shall now extend this scenario to include all higher lying states of the corresponding multiplets $|s, m\rangle$ (see Fig. 3). We shall show that this results in a fine structure for the current steps which would be resolvable only for very low temperatures [28] and hence would not be expected to be observable in DGR’s present measurements. Moreover, we find that the Zeeman splitting of resonances is strongly suppressed for a large spin $s_0 \gg 1$.

Fig. 3 illustrates the transitions between different spin wave states of “neighboring” multiplets. For simplicity, we assume that both the magnetic field and the easy axis lie in the z-direction, so that the selection rule $|m_f - m_i| = 1/2$ holds.

We solved Eq. (10) numerically for a spin [28] of $s_0 = 10$ and a Coulomb blockade region of $7 \text{eV}/s_0$ [as in Fig. 2, sample 3 of Ref. 3], and calculated the current for zero magnetic field [Fig. 3(a-c)], and non-zero applied field [Fig. 3(d-f)].

Fig. 3(a) shows the current as function of energy ($B_L eV$) for a temperature of $T = 80 \text{mK}$ and zero magnetic field, $h = 0 \text{ eV}$. The current displays seven equally spaced steps. These steps belong to transitions between successive sets of pairs of multiplets,
e.g., the first one belongs to transitions between $|s_0, m⟩$ and $|s_0 - 1/2, m⟩$, the next one to transitions between $|s_0 - 1, m⟩$ and $|s_0 - 3/2, m⟩$, etc. Fig. 3(b) shows the fourth current step of (a) on a finer energy scale. In Fig. 3(c) the same step is shown for a lower temperature of $T = 0.8$ mK, at which it now reveals sub-structure in the form of 14 finer steps. These small steps correspond to transitions between various states of the two multiplets, $|s_0 - 3, m⟩$ and $|s_0 - 7/2, m⟩$, namely the first small step in (c) corresponds to a transition, $|s_0 - 3, ±(s_0 - 4)⟩ → |s_0 - 7/2, ±(s_0 - 7/2)⟩$, the next one to $|s_0 - 3, ±(s_0 - 5)⟩ → |s_0 - 7/2, ±(s_0 - 9/2)⟩$, etc. The last step in (c) corresponds to $|s_0 - 3, ±(s_0 - 3)⟩ → |s_0 - 7/2, ±(s_0 - 7/2)⟩$. It can be checked easily, using Eq. 2, that their spacing is given by $k_N/s_0 [≈ 0.01 \text{meV}/s_0]$. Similarly, all other steps of (a) (except for the first one) have a substructure of smaller steps belonging to all transitions between neighboring multiplets that are allowed by the selection rules (as indicated in Fig. 3). Note that the number of (large-scale) steps in (a) is still given by Eq. 2(d) of Sec. VII.B with a spacing given by $d_{min} = U/2 [≈ 0.2 \text{eV}/s_0]$.

In Figs. 3(d) to (f) a similar set of plots is shown as in Figs. 3(a) to (c), but now in the presence of an applied magnetic field, $h = 0.05$ meV. Fig. 3(d) shows the current itself. Figs. 3(e) and (f) again show the fourth current step for two different temperatures. Fig. 3(e) shows that the step of (b) has Zeeman-split into two steps and (f) shows that these two steps correspond to two groups of transitions, namely all $S^z$-increasing transitions (steps on the left side) and $S^z$-decreasing transitions (right side) between the two multiplets $|s_0 - 3, m⟩$ and $|s_0 - 7/2, m⟩$. The fact that (f) shows many more steps than (c) results from the fact that the applied magnetic field lifts the degeneracy of states $|s, ±m⟩$. The first step in (f) belongs to a transition $|s_0 - 3, s_0 - 4⟩ → |s_0 - 7/2, s_0 - 7/2⟩$ the next one to $|s_0 - 3, s_0 - 5⟩ → |s_0 - 7/2, s_0 - 9/2⟩$, etc. The last step corresponds to $|s_0 - 3, s_0 - 3⟩ → |s_0 - 7/2, s_0 - 7/2⟩$.

Since the individual substeps in Fig. 3(f) are higher for the $S^z$-decreasing transitions (to the right of the plot) than for the $S^z$-increasing transitions (to the left), the second large-scale step in Fig. 3(e) is higher than the first. The reason for this height difference lies in the fact that matrix elements for transitions between different spin wave states contain Clebsch-Gordan coefficients: Let us consider the two multiplets which give rise to the current steps in Fig. 3(f), namely the $(s_0 - 3)$ and the $(s_0 - 7/2)$-multiplet. The energy levels of these multiplets are schematically depicted in Fig. 4. The first transition between the multiplets which becomes possible as the applied voltage is increased is a $S^z$-increasing transition, namely $|s_0 - 3, s_0 - 4⟩ → |s_0 - 7/2, s_0 - 7/2⟩$-transition at the bottom of the ladder. As the voltage is increased further and more $S^z$-increasing transitions become possible. (In Fig. 4 they are numbered as 1,2,⋯,2s_0 − 6.) The last $S^z$-increasing transition, namely $|s_0 - 3, -(s_0 - 3)⟩ → |s_0 - 7/2, -(s_0 - 7/2)⟩$, lies at the top of the ladder. As we increase the applied voltage further, the first $S^z$-decreasing transition $(s_0 - 3, -(s_0 - 4)) → |s_0 - 7/2, -(s_0 - 7/2))$ becomes possible (at the top of the ladder). As we increase the voltage further and more $S^z$-decreasing transitions become possible, the last transition $(s_0 - 3, s_0 - 3) → |s_0 - 7/2, s_0 - 7/2)⟩$ lying at the bottom of the ladder. Let us now compare Clebsch-Gordan coefficients involved in the different transitions. In Fig. 4 their magnitude is schematically indicated by the width of the arrows marking the transitions. For example, the Clebsch-Gordan coefficient involved in the matrix element for the first $S^z$-increasing transition $(s_0 - 3, s_0 - 4) → |s_0 - 7/2, s_0 - 7/2⟩$ as well as the first $S^z$-decreasing transition $(s_0 - 3, -(s_0 - 4)) → |s_0 - 7/2, -(s_0 - 7/2))$ in Fig. 4(f) and Fig. 4(e) is of order $O(1/s)$, hence these transitions carry very little weight. By increasing the applied voltage, so that more transitions become accessible, the Clebsch-Gordan coefficients for $S^z$-increasing transitions increase from $O(1/s)$ to $O(1)$ as we go up the ladder and those for $S^z$-decreasing transitions likewise increase from $O(1/s)$ to $O(1)$ as we subsequently go down the ladder. Now, the occupation probabilities $P_i$ in general, are larger for lower lying spin wave states than for higher-lying ones. Since transitions out of these more strongly-populated lower lying states of the spin-$(s_0 - 3)$-multiplet have a Clebsch-Gordan coefficient of order $O(1)$ if they are $S^z$-decreasing, and of order $O(1/s)$ if they are $S^z$-increasing, we conclude that the total weight of all $S^z$-decreasing transitions is larger than that of all $S^z$-increasing transitions. The net result is that the $S^z$-decreasing step in Fig. 4(e) is higher than the $S^z$-increasing step. The relative heights of the two large-scale steps in Fig. 4(e) are analyzed in Fig. 5, or more precisely, the *Fig. 7: (a) A Zeeman-split current step, where $\Delta I_{\text{decreasing}}$ is the overall height of steps due to all $S^z$-decreasing transitions and $\Delta I = \Delta I_{\text{decreasing}} + \Delta I_{\text{increasing}}$ is the overall current step. (b) $\Delta I_{\text{decreasing}}/\Delta I$, calculated numerically for various $s_0$-values for the second step in the current and $\Gamma^L/\Gamma^R = 0.1$. 
height of the current step due to all $S^z$-decreasing transitions. $\Delta I_{\text{decreasing}}$, relative to the total height of the current step $\Delta I$. Fig. 7 confirms that $S^z$-decreasing transitions typically carry significantly more weight than $S^z$-increasing transitions. Moreover, with increasing spin $S_0$ the height of $\Delta I_{\text{decreasing}}$ increases strongly relative to $\Delta I$, so that for large $S_0$ no Zeeman splitting is expected.

Let us now summarize the consequences of the nonequilibrium scenario discussed above for the tunneling spectra measured by DGR. (i) Firstly, the temperature in DGR’s experiments, namely $T \approx 80$ mK, is too large for the fine current steps of Fig. 3(c) and (f) due to spin wave excitations to have been observable. Instead, only the large-scale current steps of Fig. 3(a) and (d) would be observable. The observed resonance spacing of $\delta E_{\text{res}} \approx 0.2$ meV [cf. (P1)] indeed does agree with that expected for minority-electron charging transitions and $S_0 \approx 1000$ [cf. Eq. (19)]. (ii) Secondly, the nonequilibrium scenario discussed above can also account for the fact (P3) that the vast majority of the observed transitions within a given sample shift in energy with a similar slope for large magnetic fields, since for $S_0 > 1$, $S^z$-decreasing transitions carry far more weight than $S^z$-increasing transitions [Fig. 3].

**D. Spin and single particle excitations**

We saw in Secs. VB and VC that a nonequilibrium scenario involving transitions between different spin states (spin wave states) of the grain lead to resonances in tunneling spectra spaced by $d_{\text{min}} - U/2$, which for $S_0 = 1000$ gives a value of $0.2$ meV, as observed in experiments. However, these scenarios are not always able to explain the large number of resonances observed, since $n_{\text{res}}^\text{obs}$ given in Eq. (23) depends strongly on the threshold charging energy and can become as small as two when $E_{\text{C}}^{\text{thresh}}$ is of order or smaller than $d_{\text{min}}$.

We shall now argue below that the abundance of resonances measured by DGR can be explained by taking the analysis one step further, namely by including single-particle excitations in addition to spin excitations. For the spin excitations we shall henceforth restrict our considerations to transitions between spin ground states as in Sec. VB, since we saw in Sec. VC that DGR’s experimental temperature was too high to resolve the fine structure due to spin wave transitions. Furthermore, we shall assume $\Gamma^{\text{el}} \gg \Gamma^{\text{tun}}$, and hence shall take into account only excited single particle states involving a single particle-hole pair, i.e. states which can be reached from the corresponding ground states by a single tunneling transition, namely a majority/minority electron entering the $N$-electron grain or a majority/minority electron leaving the $N+1$-electron grain. Fig. 8 illustrates some examples.

We solved Eq. (10) numerically for the parameters of Fig. 1 in Ref. 2 and calculated the current; the result is shown in Fig 1(b). The current shows 16 steps in the plotted region. Note that the calculation of the current was done for the same parameters as in Fig. 1(a) where only spin excitations were taken into account. The arrows in (b) mark all additional resonances with respect to (a) which arise due to a combination of spin- and single particle excitations. Most of the resonances in Fig. 1(b)
FIG. 10: Resonances as function of $E^\text{thresh}_C$ and $eV_B$ for the same parameters as Fig. 4. As $E^\text{thresh}_C$ is increased additional resonances appear.

are due to tunneling of minority electrons, namely 14 resonances out of 16. This results from the very different density of states of minority and majority electrons at the Fermi energy [cf. (P4)].

Thus, when single-particle excitations are considered in addition to nonequilibrium spin accumulation, additional resonances appear at higher voltages, so that the number of resonances increases significantly. The resonances are no longer equally spaced, as was the case for pure spin excitations, but the average spacing is of the same order of magnitude.

We also investigated the gate-voltage dependence of these resonances. Fig. 10 shows resonances as function of bias voltage ($eV_B$) and threshold charging energy $E^\text{thresh}_C$. Note that $E^\text{thresh}_C$ depends linearly on gate volt-

age via Eq. 2. Fig. 10 shows clearly that the number of resonances increases with increasing $E^\text{thresh}_C$ [cf. (P5)]. This is in qualitative agreement with experimental data [Fig. 3(a) in Ref. 2], although a detailed understanding of the observed gate voltage dependence of resonances would require a more systematic examination.

VI. CONCLUSIONS

In summary, we have shown that nonequilibrium spin and single-particle excitations within our model are able to explain most of the experimental data by DGR on tunneling spectroscopy of ultrasmall ferromagnetic grains. Nonequilibrium spin excitations lead to a resonance spacings and an absence of Zeeman splitting as observed in experiments. By taking single-particle-excitations into account in addition to spin excitations, it is possible to satisfactorily explain the large number of resonances observed in experiment.

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16. A model similar in spirit was introduced independently by Canali and MacDonald.

17. A more general form for the anisotropy of an ultrasmall ferromagnetic grain would be $H_{\text{anis}} = -\sum_{ab} \sum_{ij} S_{ij}^a K_{ij}^{ab} S_{ij}^b$, where $K_{ij}^{ab}$ is a hermitian, traceless tensor.\[\sum_a K_{ij}^{aa} = 0].
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23. For DGR's Co nanograins of Ref. 1 or Ref. 2, we estimate $\Gamma^{\text{un}}$ from the conductance to be $\Gamma^{\text{un}} \approx Gd_{\text{min}}/e^2 \approx 10^9 \text{s}^{-1}$ or $10^7 \text{s}^{-1}$, respectively. By comparison, we estimate the rate for spin-conserving electronic relaxation to be $\Gamma^{\text{el}} \approx 10^7 \text{s}^{-1}$, if we use Eq.(8) of Ref. 22 (though it is not entirely clear that that formula, derived for ordinary metals, is also applicable to a strongly correlated ferromagnetic system such as Co). Thus, for the grains of Ref. 1 or Ref. 2, $\Gamma^{\text{el}}$ is of the same order or larger than $\Gamma^{\text{un}}$. As to the spin-flip rate $\Gamma^{\text{sf}}$, we do not know of a reliable way to estimate it from theoretical considerations, except to state that it is expected to be much smaller than the non-spin-flip relaxation rate, $\Gamma^{\text{el}} \ll \Gamma^{\text{sf}}$. The condition for the occurrence of nonequilibrium spin accumulation, namely $\Gamma^{\text{un}} > \Gamma^{\text{sf}}$, would thus readily be satisfied for Ref. 1, but for Ref. 2 one would need $\Gamma^{\text{sf}}$ to be more than two orders of magnitude smaller than our estimate for $\Gamma^{\text{el}}$. This difference is rather large, but might also indicate that our estimate for $\Gamma^{\text{el}}$ is unreliable large.

24. We do not consider $\mathcal{H}_{\text{uni}}$ or $\mathcal{H}_{\text{Zee}}$ here, since in DGR’s experiments the relevant energy scales, $k_N \approx 0.01 \text{meV}$ and $h_{\text{max}} \approx 0.5 \text{meV}$, are much smaller than the exchange splitting of majority and minority bands, $\Delta \epsilon \approx 2 \text{eV}$ in Co.

25. For general values of $d_{\text{min}}$, $d_{\text{max}}$, and $U$, one of the resonance spacings in $d_{\text{max}} - U/2$ in Eq. (18c) could become negative. However, only positive resonance spacings lead to observable conductance resonances. Thus, if $d_{\text{min}} - U/2 < 0$ (or $d_{\text{max}} - U/2 < 0$), only transitions involving the tunneling of majority (or minority) electrons would lead to observable conductance resonances. Note, though, that the stability condition Eq. (18a) precludes both energy differences being negative at the same time.

26. The ground state spin of $s_0 = 10$ chosen here is of course unrealistically small, but for larger values the numerical analysis becomes intractably complicated. We do believe, though, that the conclusions drawn from our numerical analysis are generic.

27. For simplicity we have not included excited single-particle states which can only be reached from ground states by multiple (nonequilibrium) excitations. However, these transitions certainly exist as $\Gamma^{\text{el}} \approx \Gamma^{\text{un}}$ (see Ref. 24) and would lead to additional resonances. Our aim, however, is to show that even by including only part of the single-particle-excitations possible, the number of resonances is increasing significantly [with respect to $n_{\text{ch}}$ given by Eq. (24)], making it possible to explain the large number of resonances in DGR’s measurements.

28. For a spin of $s_0 = 1000$ this fine structure would only be resolvable for $T < 0.2 \text{mK}$. This follows from a comparison of the spacing of the fine structure steps, $k_N/s_0$, with $k_B T$.

29. Though this statement is of course somewhat of an oversimplification, since the occupation probabilities depend in a sensitive way on the transition matrix elements, we do believe that it is, ultimately, the reason why in our numerical calculations [Fig. 6] the total weight of $S^z$-increasing transitions turns out to be much larger than for $S^z$-decreasing transitions. Note also, that in the calculation for Fig. 6 the total weight of non-relaxation processes were taken into account, which of course is not realistic. In particular, in the presence of relaxation it is to be expected that states with negative $S^z$-eigenvalues, which, loosely speaking correspond to a spin-vector pointing in a direction opposite to the applied magnetic field, would have little or no occupation probability. However, we believe that our qualitative discussion of the role of Clebsch-Gordan coefficients above would still be valid for non-zero relaxation since a non-zero relaxation would simply lead to an even larger occupation probability for the low lying spin wave states and smaller occupation probability for the high lying states. Therefore, we expect the inclusion of non-zero relaxation to make the ratio $\Delta I_{\text{decreasing}}/\Delta I$ even larger and the width of the plateau between the $S^z$-increasing and $S^z$-decreasing steps in Fig. 6(e) wider.

30. G. Pacchioni and N. Rösch, Acc. Chem. Res. 28, 390 (1995), and references therein.