Electron and Nuclear Spin Dynamics in Antiferromagnetic Molecular Rings

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We study theoretically the spin dynamics of antiferromagnetic molecular rings, such as the ferric wheel Fe_{10}. For a single nuclear or impurity spin coupled to one of the electron spins of the ring, we calculate nuclear and electronic spin correlation functions and show that nuclear magnetic resonance (NMR) and electron spin resonance (ESR) techniques can be used to detect coherent tunneling of the Néel vector in these rings. The location of the NMR/ESR resonances gives the tunnel splitting and its linewidth an upper bound on the decoherence rate of the electron spin dynamics. We illustrate the experimental feasibility of our proposal with estimates for Fe_{10} molecules.

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Magnetic molecular clusters have been the subject of intense research in recent years, because they offer the possibility of observing macroscopic quantum phenomena [1]. Ring systems such as the antiferromagnetic (AF) ferric wheels, Fe_6 and Fe_{10} [2–4], also allow one to study the transition from microscopic magnetism to one-dimensional bulk magnetism. In ferromagnetic clusters such as Fe_8 and Mn_{12}, incoherent tunneling of the $S = 10$ magnetic moment is observed directly in magnetization and susceptibility measurements [5,6]. The AF ferric wheels are candidates for the observation of macroscopic quantum coherence in the form of coherent tunneling of the Néel vector [7]. Although quantum effects in antiferromagnets are expected to be more pronounced than in ferromagnets [7,8], the detection of quantum behavior is experimentally more challenging. The reason for this is that magnetization and susceptibility measurements probe only the total spin of the molecule which, by symmetry, remains unaffected upon tunneling of the Néel vector $\mathbf{n}$. At low temperatures, the dynamics of $\mathbf{n}$ is determined by two characteristic frequencies, the tunneling rate $\Delta/\hbar$ and the electron spin decoherence rate Γ_S. In Fe_{10}, Δ can be tuned from 0 to 2 K by varying the magnetic field [7]. Although the tunnel splitting Δ enters thermodynamic quantities such as magnetization and specific heat, no conclusive results revealing the characteristic functional dependence $\Delta(B)$ have yet been obtained [9]. Measuring Γ_S is of central importance for the characterization of the quantum tunneling, since *coherent* quantum tunneling requires $\Gamma_S \lesssim \Delta$. An estimate of Γ_S can be obtained from the typical energy scales of various interactions leading to decoherence. Spin-phonon interactions are frozen out at low T. Nuclear dipolar (0.1 mK) and hyperfine (1 mK) interactions are significantly smaller than interring electron spin dipolar interactions (some 10 mK). These numbers indicate that, in Fe_{10}, tunneling of $\mathbf{n}$ is coherent for a wide range of Δ.

Motivated by these numbers, in this paper we study the quantum spin dynamics of the ferric wheel. We show that the tunnel dynamics of $\mathbf{n}$ enters the correlation functions of a *single* electron spin. As indicated in [10] for a bulk AF system, a nuclear spin coupled to a single electron spin acts as a local spin probe. We show that, in small AF rings in which $\mathbf{n}$ itself has additional coherent dynamics, the correlation functions of the nuclear spin exhibit signatures of the tunneling of $\mathbf{n}$. In particular, we discuss the coherent dynamics of one nuclear spin coupled to one of the electron spins of the ferric wheel and show that both the tunnel splitting Δ and the electron spin decoherence rate can be obtained from NMR and ESR spectra.

The ferric wheels Fe_6 and Fe_{10} are well characterized [2,3,11,12]. The $s = 5/2$ Fe III ions are arranged on a ring, with an AF nearest-neighbor exchange coupling $J > 0$ and a weak, easy-axis anisotropy directed along the ring axis $\mathbf{e}_z$. The minimal Hamiltonian for the system is

$$H_0 = J \sum_{i=1}^{N} \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \mathbf{h} \cdot \sum_{i=1}^{N} \mathbf{s}_i - k_z \sum_{i=1}^{N} s_{i,z}^2, \quad (1)$$

where $N = 10$ or 6 and $\mathbf{s}_{N+1} \equiv \mathbf{s}_1$, $\mathbf{h} = g\mu_B \mathbf{B}$, with $\mathbf{B}$ the external magnetic field and $g = 2$ the electron spin g-factor. For Fe_{10}, $J = 15.56$ K and $k_z = 0.0088J$. For Fe_6, the values for J and k_z vary appreciably depending on the central alkali metal atom: for Na:Fe_6, $J = 32.77$ K and $k_z = 0.0136J$, whereas, for Li:Fe_6, $J = 20.83$ K and $k_z = 0.0053J$ [11,13].

For $k_z = 0$, the eigenstates of H_0 are also eigenstates of the operator of total spin, $\mathbf{S} = \sum_{i=1}^{N} \mathbf{s}_i$, with $E_{S,S_x} = (2J/N)S(S+1) + hS_x$ [2]. For $k_z \ll 2J/(Ns)^2$, the anisotropy can be taken into account in perturbation theory in k_z. The scenario changes drastically for $k_z \gtrsim 2J/(Ns)^2$, when $\mathbf{n}$ (staggered magnetization) is localized along $\pm\mathbf{e}_z$. We label the states with $\mathbf{n}$ oriented along $\pm\mathbf{e}_z$ by $|\Uparrow\rangle$ and $|\Downarrow\rangle$. In a semiclassical description, the low-energy sector of the ferric wheel consists of two states, a ground state, $|g\rangle = (|\Uparrow\rangle + |\Downarrow\rangle)/\sqrt{2}$, and a first excited state, $|e\rangle = (|\Uparrow\rangle - |\Downarrow\rangle)/\sqrt{2}$. The static equilibrium properties of a system described by Eq. (1) are discussed in detail in Ref. [7]. With $\mathbf{B} \parallel \mathbf{e}_x$, i.e., in the plane of the ring, the system exhibits interesting spin dynamics: In the high field regime, $h_x \gg \hbar\omega_0$, $\mathbf{n}$ is confined to the (y,z) plane and tunneling takes place through the potential barrier of height $Nk_z s^2$. In particular, $\Delta = \Delta_0 |\sin(\pi N h_x/4J)|$, with $\Delta_0 = 8\hbar\omega_0\sqrt{S/2\pi\hbar}\, e^{-S/\hbar}$, $\omega_0 = s\sqrt{8Jk_z}/\hbar$, and $S/\hbar = Ns\sqrt{2k_z/J}$, shows oscillatory behavior as a function of h_x [7]. We restrict our considerations henceforth to the geometry $\mathbf{B} \parallel \mathbf{e}_x$. For Fe_{10}, $\Delta_0 \simeq 2.18$ K is much larger than in, e.g., Mn_{12} [14,15] or Fe_8.

Spin susceptibilities.—We consider first the standard ac spin susceptibility and ESR measurements, in which an infinitesimal magnetic probing field couples to the total spin $\mathbf{S} = \sum_{i=1}^{N} \mathbf{s}_i$ of the ferric wheel. We will show that these experimental techniques are insufficient to detect coherent tunneling of $\mathbf{n}$ in a system described by H_0 alone. In an effective-action description for the system (1) with Lagrangian density $L_E[\mathbf{n}]$ [7], we find $\mathbf{S} = \frac{N}{4J}[i\mathbf{n} \times \dot{\mathbf{n}} - \mathbf{h} + \mathbf{n}(\mathbf{n} \cdot \mathbf{h})]$. In high magnetic fields $h_x \gg \hbar\omega_0$, the spin susceptibility, $\chi_{\alpha\alpha}(\omega) = \int_0^{\beta\hbar} d\tau \langle T_\tau \hat{S}_\alpha(\tau)\hat{S}_\alpha\rangle e^{i\omega_n\tau}|_{i\omega_n \to \omega + i0}$, with $\alpha = x, y, z$, $\beta = 1/k_B T$, and T_τ the imaginary time ordering operator, may be evaluated using spin path integrals. For $\omega, k_B T/\hbar \ll \omega_0, h_x/\hbar$, up to corrections $\mathcal{O}(e^{-S/\hbar})$,

$$\chi_{\alpha\alpha}(\omega) = \frac{N}{4J} f_\alpha\,, \tag{2}$$

with $f_x = 1 - \mathcal{O}(\pi^2 N\Delta/8J)$ and $f_y \simeq f_z \simeq 1$. It is clear from Eq. (2) that the susceptibilities $\chi_{\alpha\alpha}(\omega)$ for the ring (1) do *not* exhibit resonances at $\omega = \pm\Delta/\hbar$. The main conclusion we draw from Eq. (2) is that a uniform magnetic field cannot drive transitions from $|g\rangle$ to $|e\rangle$. Starting from the rigid rotor Hamiltonian of the ferric wheel [7], this result can also be shown to hold for an arbitrary direction of $\mathbf{B}$.

We now consider the correlation function of a *single spin*, $\langle T_\tau \hat{s}_{i,\alpha}(\tau)\hat{s}_{i,\alpha}\rangle \simeq s^2\langle T_\tau n_\alpha(\tau) n_\alpha\rangle$, for $h_x \ll 4Js$, with $i = 1, \ldots, N$. In contrast to the correlations of $\mathbf{S}$ discussed above, $\langle T_\tau \hat{s}_{i,\alpha}(\tau)\hat{s}_{i,\alpha}\rangle$ indeed exhibits signatures of coherent tunneling of $\mathbf{n}$. To evaluate the correlation function, we use an effective two-state description for the ferric wheel and introduce a pseudospin $\hbar\boldsymbol{\sigma}/2$, with $|\uparrow\rangle$ and $|\downarrow\rangle$ being eigenstates of σ_z. The tunneling dynamics of the Néel vector $\mathbf{n}$ is then generated by the pseudo-Hamiltonian $-\Delta\sigma_x/2$. Because $\langle T_\tau n_z(\tau) n_z\rangle \simeq \langle T_\tau \sigma_z(\tau)\sigma_z\rangle$ in the low-energy sector, we obtain immediately

$$\langle T_\tau \hat{s}_{i,z}(\tau)\hat{s}_{i,z}(\tau')\rangle \simeq s^2 \frac{\cosh[(\beta - 2|\tau - \tau'|)\Delta/2]}{\cosh[\beta\Delta/2]}\,. \tag{3}$$

After analytic continuation, the real-time correlation function exhibits the $e^{\pm i\Delta t/\hbar}$ time dependence characteristic of coherent tunneling. We conclude that *local* spin probes allow the observation of the Néel vector dynamics. Nuclear spins which couple (predominantly) to a given $\mathbf{s}_i$ are ideal candidates for such probes, as we shall discuss next.

Nuclear susceptibility.—NMR techniques have been widely used to study molecular magnets [16,17]. In the following we show that nuclear spins can also be used as a local probe to detect coherent tunneling of $\mathbf{n}$. For simplicity, we restrict our considerations to interactions of the form $H' = A\mathbf{s}_1 \cdot \mathbf{I}$, which includes both the hyperfine contact interaction and the direction-independent part of the magnetic dipolar interaction. For $^{57}\mathrm{Fe}$, the dominant coupling to the electron spin is by a hyperfine contact interaction, $A_{\mathrm{Fe}} s \simeq 3.3$ mK [18]. In contrast, the interaction of a $^{1}\mathrm{H}$ nuclear spin with the electron spins is dipolar, with a direction-independent term $\sum_i A_i \mathbf{s}_i \cdot \mathbf{I}$. For AF order, the sum yields an effective coupling $A_{\mathrm{H}} s\mathbf{n} \cdot \mathbf{I}$, where, for Fe_{10}, the coefficient $A_{\mathrm{H}} = \sum_i (-1)^{i+1} A_i$ depends strongly on the site of the proton spin $\mathbf{I}$. For many of the inequivalent sites, however, A_{H} is of order 0.1 mK [17]. With N_{Fe} and N_{H} the numbers of NMR-active $^{57}\mathrm{Fe}$ and proton nuclei, as long as $N_{\mathrm{Fe}} A_{\mathrm{Fe}} + N_{\mathrm{H}} A_{\mathrm{H}} \ll \Delta$, the effect of the nuclear spins on the electron spin dynamics remains small. We define the decoherence rates Γ_I and Γ_S of the nuclear and electronic spins as the decay rates of $\langle I_y(t) I_y\rangle$ and $\langle n_z(t) n_z\rangle$, respectively. For time scales $t < 1/\Gamma_S$, the electron spin produces a coherently oscillating effective magnetic field with frequency $\Delta/\hbar$ at the site of the nucleus.

In order to show that this field affects the nuclear spin dynamics, we now consider a single, NMR-active $^{57}\mathrm{Fe}$ or $^{1}\mathrm{H}$ nucleus (inset of Fig. 1). For $k_B T \ll \hbar\omega_0$, we may restrict our considerations to the Hilbert space spanned by $\{|g\rangle, |e\rangle\}$. By using the decomposition $\mathbf{s}_i = (-1)^{i+1} s\mathbf{n} + \mathbf{S}/N$ of a single spin into staggered magnetization $\pm s\mathbf{n}$, $\mathbf{n}^2 = 1$, and fluctuations $\mathbf{S} \perp \mathbf{n}$ around the Néel ordered state, we obtain $H' = A\mathbf{s}_1 \cdot \mathbf{I} \simeq As\mathbf{n} \cdot \mathbf{I}$. We show now that, due to $\langle e|n_z|g\rangle \neq 0$, the tunneling dynamics of $\mathbf{n}$ can be obtained from the nuclear spin correlation functions

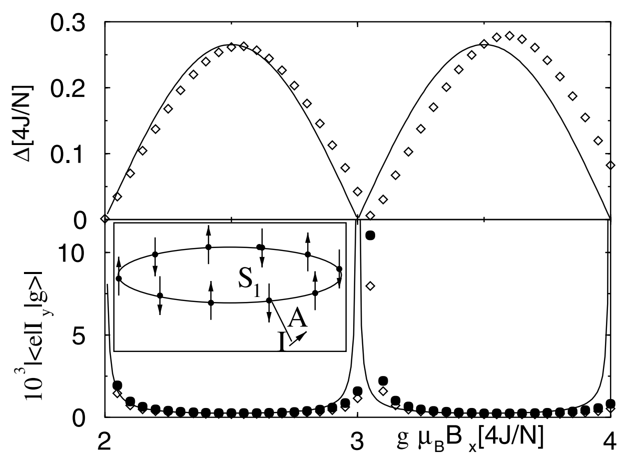

FIG. 1. Comparison of the analytical result for Δ (upper panel) and $\langle e|I_y|g\rangle$ (lower panel) with exact numerical results for a small system, $N = 4$, $s = 3/2$, $k_z = 0.2J$, and $A = 9 \times 10^{-5}J$. The numerical values ($\diamond$) for $\langle e|I_y|g\rangle$ are well approximated by $As/2\Delta$ (solid line), with a small offset in B_x resulting from the shift of the magnetization steps when $k_z \neq 0$. For reference, the ratios $As/2\Delta$ with the numerical values for Δ are shown ($\bullet$) in the lower panel.

$\langle I_\alpha(t) I_\alpha \rangle$. With $\langle e|n_z|g\rangle = \mathcal{O}(1)$, the dominant term in H' is $Asn_z I_z$ or, in the pseudospin notation introduced above,

$$H' \simeq Asn_z I_z \simeq As\sigma_z I_z \,. \tag{4}$$

NMR experiments measure via power absorption the imaginary part of the nuclear spin susceptibility, $\chi''_{I,\alpha\alpha}(\omega)$, and by pulsed techniques the nuclear spin correlation functions $\langle I_\alpha(t) I_\alpha \rangle$ in the time domain [19]. From expanding $\langle I_\alpha(t) I_\alpha \rangle$ in H',

$$\langle I_\alpha(t) I_\alpha \rangle \simeq \langle I_\alpha(t) I_\alpha \rangle_0 - A^2 s^2/\hbar^2 \int_{-\infty}^{t} dt' \int_{-\infty}^{0} dt'' \times \langle [I_z(t'), I_\alpha(t)][I_z(t''), I_\alpha]\rangle_0 \langle n_z(t') n_z(t'')\rangle_0 \,, \tag{5}$$

it is evident that the dynamics of $\mathbf{n}$ enters $\chi''_{I,\alpha\alpha}(\omega)$.

To evaluate Eq. (5), we diagonalize the Hamiltonian

$$H = -\frac{\Delta}{2}\sigma_x + \gamma_I B_x I_x + AsI_z\sigma_z \,, \tag{6}$$

with γ_I the nuclear gyromagnetic ratio, which describes the ferric wheel in the low-energy sector with a single nuclear spin $\mathbf{I}$ coupled to $\mathbf{s}_1$ [Eq. (4)]. We assume thermal equilibrium for both electron and nuclear spins. For Fe_{10} in the high field regime, the results may be derived by expansion to leading order in As/Δ and $\gamma_I B_x/\Delta$, because $\Delta_0 \gg \gamma_I B_x, As$, for both ^{57}Fe and ^{1}H nuclei, and $B_x \simeq 10$ T. For $I = 1/2$, $\chi''_{I,zz}(\omega)$ displays the unperturbed emission and absorption peaks at $\omega \simeq \pm\gamma_I B_x/\hbar$, although these are slightly shifted if the hyperfine term $A\mathbf{S}\cdot\mathbf{I}/N$ is taken into account. $\chi''_{I,xx}(\omega)$, however, displays resonant absorption and emission of small intensity at $\omega = \pm(\Delta \pm \gamma_I B_x)/\hbar$. Finally,

$$\chi''_{I,yy}(\omega) = \frac{\pi}{4}\left[\tanh\left(\frac{\beta\gamma_I B_x}{2}\right)\delta(\omega - \gamma_I B_x/\hbar) + \left(\frac{As}{\Delta}\right)^2 \tanh\left(\frac{\beta\Delta}{2}\right)\delta(\omega - \Delta/\hbar)\right] - [\omega \to -\omega] \tag{7}$$

exhibits *satellite resonances at the tunnel splitting* Δ *of the electron spin system.* Their physical origin is readily understood in terms of a classical vector model. For $A = 0$, $\mathbf{I}(t)$ precesses around the static magnetic field $\mathbf{B} = B_x\mathbf{e}_x$. For $A \neq 0$, the coherent tunneling of $\mathbf{n}$ leads to an additional ac hyperfine field $A\mathbf{s}_1(t) \simeq As\cos(\Delta t/\hbar)\mathbf{e}_z$ at the site of the nucleus. In contrast to a static hyperfine field which induces a change in precession frequency and axis, the rapidly oscillating hyperfine field in Fe_{10} leads only to a small deviation $\delta\mathbf{I}(t) = \mathcal{O}(As/\Delta)$ from the original precession. In particular, $\delta I_y(t) \propto (As/\Delta)\sin(\Delta t/\hbar)$ also oscillates at frequency $\Delta/\hbar$ and hence gives rise to the second term in Eq. (7).

We restricted the above analysis to the low-energy sector of the ferric wheel. To check this approximation, we performed exact numerical diagonalization (ED) on a small AF ring with one nuclear spin of $I = 1/2$ coupled to one of the electron spins. For the small systems accessible by ED, in this case $N = 4$, $s = 3/2$, and $k_z = 0.2J$, the field range for which the theoretical framework is applicable becomes rather small: $2J \ll h_x \ll 6J$. However, the numerical results (Fig. 1) for $\langle e|I_y|g\rangle$ indicate that our analytical value $|\langle e|I_y|g\rangle| = As/2\Delta$ entering Eq. (7) is a good approximation. For our parameters, the analytical value tends to overestimate $\langle e|I_y|g\rangle$ by $\sim$30% which results from the neglect of n_y in Eq. (4).

We turn next to a discussion of the experimental feasibility of measuring Δ by NMR. Because $As/\Delta \ll 1$, the intensity of the satellite peaks at $\omega = \pm\Delta/\hbar$ (7) is small compared to that of the main peaks at $\omega = \pm\gamma_I B_x/\hbar$. However, this satellite peak intensity may be increased significantly by tuning B_x close to one of the critical values B_x^c at which the magnetization of the ferric wheel jumps and $\Delta(B_x = B_x^c) = 0$. Note, however, that our theory applies only to high magnetic fields, $B_x > 7.7$ T for Fe_{10}. Coherent tunneling of the Néel vector $\mathbf{n}$ requires $\Delta \gtrsim \Gamma_S$. From the estimates for the decoherence rate Γ_S given earlier, we conclude that this condition can be satisfied even for a large range of $\Delta/\Delta_0 \ll 1$.

We consider first ^{57}Fe, with $\gamma_I = 0.18\mu_N$ [20]. For $T \simeq 2$ K and $B_x \sim 10$ T, the relative intensity of the satellite peak at $\Delta = \Delta_0 = 2.18$ K, is $(As/\Delta)^2\tanh(\beta\Delta/2)/\tanh(\beta\gamma_I B_x/2) \simeq 0.007$. This intensity, however, increases by a factor of 10 (100) for $\Delta = 0.1\Delta_0$ ($\Delta = 0.01\Delta_0$). For ^{1}H with $\gamma_I = 5.59\mu_N$ [20], and a typical value $As \simeq 0.1$ mK, the relative peak intensity is 2.05×10^{-7} ($\Delta = \Delta_0$), 2.25×10^{-6} ($\Delta = 0.1\Delta_0$), and 2.25×10^{-5} ($\Delta = 0.01\Delta_0$). However, the number of protons in the ring is much larger than that of NMR-active ^{57}Fe nuclei, $10 \lesssim N_H/N_{Fe} \lesssim 100$, depending on the doping with ^{57}Fe. Taking into account that the sensitivity of proton NMR is larger than that of Fe NMR by a factor of 3×10^4 [20], ^{57}Fe and proton NMR appear to be similarly appropriate for detecting the coherent tunneling of $\mathbf{n}$. The observation of the satellite peak in (7) is feasible, but still remains a challenging experimental task. The experiment must be conducted with single crystals of Fe_{10} [or a Fe_6 system with sufficiently large $k_z > 2J/(Ns)^2$] at high, tunable fields (10 T) and low temperatures (2 K). Moreover, because B_x^c depends sensitively on the relative orientation of $\mathbf{B}$ and the easy axis [11,13], careful field sweeps are necessary to ensure that $\Delta/\Delta_0 \ll 1$ is maintained [21]. Note that the NMR experiment suggested here could be more easily realized with nuclear spins exhibiting higher NMR sensitivity than ^{57}Fe.

We show now that, from NMR spectra, also an upper bound for Γ_S can be extracted. The NMR resonance lines are broadened by the decoherence of the nuclear spin, with width Γ_I at $\pm\gamma_I B_x/\hbar$. The NMR resonances at $\omega = \pm\Delta/\hbar$ also involve correlation functions of $\mathbf{n}$ [see (5)]. Thus the decoherence of the electron spin, Γ_S, adds to the linewidth, and the width of the satellite peak, δ, is bounded by $\Gamma_I + \Gamma_S < \delta$. Measurement of δ then provides an upper bound for Γ_S. Further, $\Gamma_S \simeq \Delta$ marks the transition from coherent to incoherent tunneling dynamics. Hence, if $\delta < \Delta$ this would indicate unambiguously that quantum tunneling of $\mathbf{n}$ is coherent. Note that the maximum peak height of a Lorentzian resonance line is $\mathcal{O}(1/\delta)$, so a large Γ_S ($<\Delta$) would make detection of the satellite peak increasingly difficult.

ESR measurements in the presence of hyperfine interaction.—We show now that, in the presence of a hyperfine coupling H', the electron spin susceptibility of the ring, $\chi_{\alpha\alpha}(\omega)$, also exhibits the signature of a coherent tunneling of $\mathbf{n}$. This results from the fact that integration over the initial and final nuclear spin configurations causes the matrix elements $\langle e|\mathbf{S}|g\rangle$ occurring in the spectral representation of $\chi_{\alpha\alpha}(\omega)$ [Eq. (2)] to become finite. In the high field limit $h_x \gg \hbar\omega_0$, the matrix elements become $|\langle e|S_y|g\rangle| \simeq (As/2h_x)(\Delta_0 S/4Nk_z s^2)\,|\cos(\pi N h_x/4J)|$ and $|\langle e|S_z|g\rangle| \simeq As/2h_x$. For a small system ($N = 4$, $s = 3/2$), we have again confirmed the qualitative features of these results by ED. It follows that $\chi''_{\alpha\alpha}(\omega \sim \Delta/\hbar) = \pi|\langle e|S_\alpha|g\rangle|^2 \tanh(\beta\Delta/2)\delta(\omega - \Delta/\hbar)$ exhibits resonances at $\Delta/\hbar$. A qualitative understanding of this result may be obtained by noting that a nuclear spin polarized along $\mathbf{B}$ results in an effective magnetic field $\mathbf{e}_x A/2g\mu_B$ acting only on $\mathbf{s}_1$. In a classical description this hyperfine field causes $\mathbf{S}$ to acquire a component $\mathbf{n}As/2h_x$ along $\mathbf{n}$, and the coherent tunneling of $\mathbf{n}$ now also results in an oscillation of the total spin $\mathbf{S}$. Again, the decoherence rate of these oscillations, and hence the linewidth of the ESR resonance, is bounded by Γ_S. Note that $As/2h_x = 1.2 \times 10^{-4}$ for a single ^{57}Fe nucleus with $B_x = 10$ T, so the ESR signal is very weak in this case.

However, our calculations apply to any impurity spin $\mathbf{j}$, which interacts with a single electron spin only, $H' = A\mathbf{s}_1 \cdot \mathbf{j}$. In particular, for an electronic $\mathbf{j}$, A is typically 10^3 times larger than for a nuclear spin, and ESR techniques become a valuable tool for detecting the tunneling of $\mathbf{n}$. One advantage of this technique is that it is no longer necessary to have $\Delta/\Delta_0 \ll 1$ to obtain a large signal intensity, and thus the complete range of tunnel frequencies could be explored experimentally [22]. Our calculations also apply to situations in which several impurity spins $\mathbf{j}_i$ produce different net magnetic fields for the two sublattices of the AF ring. For illustration, we discuss two simple scenarios. We consider $N/2$ impurity spins $\mathbf{j}_i$ ($j_i = 1/2$) coupled to $\mathbf{s}_1, \mathbf{s}_3, \ldots, H' = A\sum_{i=1}^{N/2} \mathbf{j}_{2i-1} \cdot \mathbf{s}_{2i-1}$. For $h_x \gg As, k_B T$, all $\mathbf{j}_i$ align with the magnetic field $\mathbf{B}$. Since they all couple to one sublattice only, their net magnetic fields acting on $\mathbf{s}_i$ add up, $|\langle e|S_z|g\rangle| \simeq (N/2)As/2h_x$, leading to a $(N/2)^2$-fold enhancement of the ESR signal of a single impurity. In contrast, a single impurity $\mathbf{j}$ coupled to both $\mathbf{s}_1$ and $\mathbf{s}_2$, $H' = A\mathbf{j} \cdot (\mathbf{s}_1 + \mathbf{s}_2)$, results in the same net magnetic field acting on both sublattices, $\langle e|S_z|g\rangle = 0$.

Conclusions.—We have shown that NMR and ESR techniques can be used to measure both the tunnel splitting Δ and the decoherence rate Γ_S in the ferric wheel. For Fe_{10}, we showed that our proposal is within experimental reach. Our considerations apply to any AF ring system described by H_0 [Eq. (1)], with some impurity spin coupled to one of the electron spins. Hence, the proposed scheme may prove useful for a wide class of molecular magnets.

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