Electron Spin Echo Envelope Modulation at Clock Transitions in Molecular Spin Qubits

Jia Chen,1,2,3 Silas Hoffman,1,2,3 Krishnendu Kundu,4 Jonathan Marbey,3,4,5 Dorsa Komijani,4,5 Yan Duan,6 Alejandro Gaita-Ariño,6 Xiao-Guang Zhang,1,2,3 Stephen Hill,3,4,5 Hai-Ping Cheng1,2,3

1Department of Physics, University of Florida, Gainesville, FL 32611, USA
2Quantum Theory Project, University of Florida, Gainesville, FL 32611, USA
3Center for Molecular Magnetic Quantum Materials
4National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA
5Department of Physics, Florida State University, Tallahassee, FL 32306, USA
6Instituto de Ciencia Molecular (ICMol), Universitat de València, Paterna, Spain
7Department of Chemistry, University of Florida, Gainesville, FL 32611, USA

Clock transitions (CTs) have been shown to protect qubits against various sources of decoherence. Here, we present a joint experimental and theoretical investigation of the decoupling of a central electron spin qubit from the surrounding nuclear spin bath by studying the so-called Electron Spin Echo Envelope Modulation (ESEEM) effect in the vicinity of a magnetic CT. Experimentally, ESEEM spectra are collected for a HoW_{10} molecular spin qubit, and suppression of the modulation at a CT is clearly demonstrated. The effect is then simulated theoretically by exact quantum time evolution using a simple model Hamiltonian of a central electron spin with an avoided Zeeman crossing coupled to a finite number of nuclear bath spins. The results reproduce key experimental observations and reveal that, due to the
quadratic energy dependence on magnetic field at the avoided crossing, fluctuations of the nuclear spin bath that couple linearly to the central spin do not affect its quantum dynamics at the CT. Consequently, hyperfine coupling effectively vanishes, leading to a complete suppression of ESEEM and electron-nuclear decoherence at the CT.

1 Introduction

Molecular spin systems represent a promising and versatile materials platform for next-generation quantum technologies. As demonstrated in several recent breakthrough studies, chemical approaches enable the design of molecules with properties tailored for specific applications, potentially opening the door to new opportunities in quantum sensing and quantum computing. Carrying out high-fidelity quantum logic operations on spins entails driving transitions between eigenstates of the static Hamiltonian, necessitating precisely controlled electromagnetic perturbations. Moreover, protection against leakage of quantum information to the environment—so-called decoherence—is of critical importance, representing one of the main hurdles on the path towards practical quantum computing applications in the near future.

Pulsed electron spin resonance (ESR) is an extremely powerful technique, enabling both characterization and quantum control of electron spin systems. Indeed, pulsed ESR is central to most electron spin quantum computing proposals. A well-known example involving quantum control is the two-pulse Hahn echo sequence, where a coherent state is first generated via a $\pi/2$ rotation on the Bloch sphere and then allowed to evolve with time; this evolution is later time-reversed via the application of a $\pi$ pulse (an inversion). The Hahn echo sequence is known
to refocus the dephasing that occurs in spin ensembles subjected to static disorder, resulting in the emission of an electron-spin-echo (ESE) at time $2\tau$ after the initial $\pi/2$ pulse (where $\tau$ is the delay between pulses). A dynamic environment causes decoherence,\textsuperscript{7} which manifests as a decay of the Hahn echo intensity upon increasing $\tau$. However, coherent interactions with nearby quantum systems, e.g., other electrons or atomic nuclei, can give rise to a modulation of the ESE intensity.\textsuperscript{6}

In particular, ESE envelope modulation (ESEEM) arises when nearby nuclear spins interact with the coherent state associated with a central electron spin via hyperfine or dipolar coupling. Here, “central” refers to a spin that has been prepared in a prescribed coherent quantum state, e.g., via the application of a $\pi/2$ pulse. In molecular magnetic materials, coupling to nuclear bath spins represents one of the more stubborn sources of dephasing. ESEEM can be used to characterize this aspect of the environment, thereby providing key insights into the leakage of quantum information to the nuclear bath.

In an attempt to suppress decoherence in molecular qubits arising from electron-nuclear magnetic coupling, various synthetic strategies have been employed, such as controlling nuclear spin patterns\textsuperscript{8,9} and the use of nuclear spin free ligands.\textsuperscript{10,11} However, demonstration of long phase memory (coherence) times still requires extreme dilution in these cases in order to minimize electron spin-spin dephasing. Rather than modifying details of the spin bath, an alternative approach involves so-called clock transitions (CTs)\textsuperscript{12} at which the qubit transition frequency is insensitive to the local magnetic induction and, therefore, does not couple to the fluctuating magnetic environment. Such transitions occur at avoided level crossings associated with the Zeeman splitting of the qubit basis states. For integer-spin Ising systems, such avoided crossings may be gener-
ated and controlled via a static transverse magnetic anisotropy \(^1\) while, for half-integer systems, the electron-nuclear hyperfine interaction serves the same role. \(^{12,13,14}\) Meanwhile, dressed states associated with driven systems may also exhibit similar physics. \(^{15}\) These approaches are well established in solid-state materials, such as donor atoms in silicon \(^{16,17}\) or defects in diamond \(^{18}\) and silicon carbide, \(^{19}\) where recent theoretical work based on a cluster-correlation expansion technique has also yielded good agreement with experiment. \(^{20}\) In molecular systems, Shiddiq et al. successfully demonstrated enhanced coherence at a CT for a \([\text{Ho}(\text{W}_{5}\text{O}_{18})_2]^{9-}\) complex. \(^{21}\) Subsequently, CTs have been studied in other molecular systems \(^{13,14,22,23,24}\) and the effects of structural distortions have been analyzed theoretically for several Ho\(^{\text{III}}\) and V\(^{\text{IV}}\) complexes. \(^{25}\)

In this study, we investigate the decoupling of a central electron spin from the surrounding nuclear bath through combined experimental and theoretical demonstrations of the absence of ESEEM at a CT. Theoretically, we consider a minimal model which can host a CT: an \(S = 1\) Ising spin subject to a significant transverse anisotropy (Fig. 1). We treat the coupling to the nuclear spin bath explicitly to directly reproduce the ESEEM effect away from the CT via quantum dynamics simulations. The theoretical results compare favorably with experimental pulsed ESR data for the \([\text{Ho}(\text{W}_{5}\text{O}_{18})_2]^{9-}\) molecule, the only system for which ESEEM has been characterized as a function of magnetic field strength in the vicinity of a CT. Although the experiments focus on \([\text{Ho}(\text{W}_{5}\text{O}_{18})_2]^{9-}\), our simplified model applies quite generally for the coupling of a central electron spin to a finite nuclear bath. The combined study provides a microscopic view of the mechanism via which a central electron spin couples to nearby nuclear spins, in essence mediating leakage of quantum information to the nuclear bath.
2 Experiment

In order to illustrate the behavior of ESEEM in the vicinity of a CT, pulsed ESR measurements were performed on a single crystal of the compound Na$_9$[Ho$_x$Y$_{1-x}$(W$_5$O$_{18})_2$]$\cdot$nH$_2$O (hereon abbreviated HoW$_{10}$), where $x = 0.001$, i.e., 0.1% HoW$_{10}$ doped into an isostructural non-magnetic YW$_{10}$ host crystal. As an extensive discussion of the experimental conditions and electronic properties that give rise to CTs in HoW$_{10}$ has been presented previously, only brief descriptions of the essential details are given here.

Ho$^{III}$ possesses a ground state spin-orbit coupled angular momentum, $J = L + S = 8$, with an $I = \frac{7}{2}$ nuclear spin. The square antiprismatic coordination geometry imposed on the Ho$^{III}$ ion by the two W$_5$O$_{18}$ moieties gives rise to a crystal field (CF) interaction that lifts the degeneracy of the $2J + 1$ projection ($m_J$) states. The pseudo-axial nature of the CF, described in terms of set of axial CF parameters, $B^q_k$ ($k = 2, 4, 6$ representing the rank of the associated CF operator, $\hat{O}^q_k$, and $q = 0$ the rotational order), gives rise to a singlet and a series of $m_J = \pm i$ ($i = 1$ to 8) quasi-doublets, with the $m_J = \pm 4$ ground doublet lying approximately 40 cm$^{-1}$ below the first excited CF states. Minor distortions away from exact $D_{4d}$ point symmetry engage the tetragonal CF interaction, $B^4_4 \hat{O}^4_4 \propto (\hat{S}^4_+ + \hat{S}^4_-)$, which is effective in generating an avoided crossing between the $m_J = \pm 4$ basis states, thus giving rise to a CT. The hyperfine interaction involving the $I = \frac{7}{2}$ $^{165}$Ho nuclear spin further splits the $m_J = \pm 4$ states into $(2I + 1) = 8$ pairs of $m_I$ sub-levels, effectively resulting in eight avoided-crossings for the HoW$_{10}$ molecule with CT frequencies, $f_{\text{min}} \approx 9.1$ GHz, at magnetic fields, $B_{\text{min}} = \pm 23.5, \pm 70.9, \pm 118$ and $\pm 165$ mT [for
an applied field, $B_0$, parallel to the molecular easy ($z$-) axis of magnetization].

ESEEM measurements were performed using a commercial spectrometer equipped with a cylindrical TE$_{011}$ dielectric resonator (unloaded center frequency of 9.75 GHz), which was overcoupled to increase bandwidth and, thus, allow measurements at frequencies down to 9.1 GHz. For reasons explained in Ref. [21], we focus here on the lowest field CT which gives the optimum coherence. A slight $\sim 23^\circ$ misalignment between the applied field and the molecular easy axis of magnetization results in the CT occurring at $B_0 = B_{\text{min}} = 25.5$ mT ($\equiv B_{0z} = 23.5$ mT).

ESE decay curves were generated using a simple two-pulse Hahn-echo sequence as a function of detuning from the CT field, $B_{\text{min}}$. Time traces recorded for a frequency of 9.18 GHz are shown in Fig. 2(a) as a function of delay time, $2\tau$, revealing strong temporal modulations—ESEEM—at most detunings. The frequency domain plots in Fig. 2(b) were obtained by performing fast Fourier transforms (FFTs) of the time traces, which were zero padded by twice the number of data points and further smoothed using a 5 point average.

The first thing to note from the time traces in Fig. 2(a) is the variation in decay time (equivalent to the phase memory time, $T_m$) and modulation depth as a function of the detuning, $B_0 - B_{\text{min}}$. Most notably, there is a complete absence of ESEEM at zero detuning, i.e., at the CT. Post data processing, three prominent peaks can be observed in the FFTs, which are highlighted by the red, green and blue circles in Fig. 2(b). The associated ESEEM frequencies are plotted as a function of the applied field strength in Fig. 2(c); superimposed on the data are the 1$^{\text{st}}$ and 2$^{\text{nd}}$ harmonics of the bare proton Larmor frequency, $\nu_H = \gamma_H B_0$, where $\gamma_H = 42.577$ MHz/T is the proton gyro-
magnetic ratio. The fact that the center-of-mass of the red/green data points coincides with $\nu_\text{H}$ and the blue data points with $2\nu_\text{H}$ is a strong indication that the ESEEM is caused by dipolar coupling to protons. This is not surprising given the significant amount of solvated water in the lattice of HoW$_{10}$ ($n \approx 35$ in fully solvated crystals). By contrast, the W and O nuclei in the molecular core are predominantly non-magnetic, with the exception of $^{17}$O ($I = \frac{5}{2}, \gamma = 5.77 \text{ MHz/T}$) and $^{183}$W ($I = \frac{1}{2}, \gamma = 1.77 \text{ MHz/T}$) with 0.04% and 14.3% natural abundance, respectively. Moreover, their associated $\gamma$-values, along with those of the more distant $^{23}$Na and $^{89}$Y nuclei (both 100% abundance), cannot be confused with that of the proton.

A strong proton ESEEM effect is expected in this field range where the Ho-$^1$H dipolar coupling strength ($\sim 0.5$ MHz for the closest protons, vide infra) is comparable to $\nu_\text{H}$ ($\sim 1.2$ MHz). A qualitative understanding is obtained by first considering the simplest possible case of coupled $S = \frac{1}{2}$ and $I = \frac{1}{2}$ spins in the high-field limit in which $\nu_\text{H} \gg A$, where $A = A_{zz}/h$, $A_{zz}$ is the $z$-component of the hyperfine tensor) quantifies the dipolar coupling strength in frequency units. ESEEM arises due to excitation of formally forbidden transitions that rotate coupled nuclear spins in addition to the electron magnetization. The modulation results from a beating of the allowed ($\nu_a = \gamma_e B_0 \pm \frac{1}{2}A$, $\gamma_e$ is the electron gyromagnetic ratio) and forbidden ($\nu_f = \gamma_e B_0 \pm \nu_\text{H}$) transition frequencies at: $|\nu_a^\pm - \nu_a^\mp| = A$, $|\nu_f^\pm - \nu_a^\pm| = |\nu_f^\mp - \nu_a^\mp| = \nu_\text{H} \pm \frac{1}{2}A$ and $|\nu_f^\pm - \nu_f^\mp| = 2\nu_\text{H}$. One may then understand the red/green data points for HoW$_{10}$ in Fig. 2(b) as being due to the hyperfine coupled proton frequencies, $\nu_\text{H} \pm \frac{1}{2}A^\text{eff}$, where $A^\text{eff}$ is an effective coupling strength on account of the new physics that emerges at the CT ($A^\text{eff}$ is also renormalized relative to the bare hyperfine coupling due to the fact that $S \neq \frac{1}{2}$). Crucially, it is apparent that $A^\text{eff} \to 0$ at the CT, which may
be understood as being a consequence of the effective electron gyromagnetic ratio, $\gamma_e^{\text{eff}}$, crossing through zero at $B_0 = B_{\text{min}}$ ($\gamma_e^{\text{eff}} \propto df/dB_0$ or $\langle \hat{S}_z \rangle$, the $z$-component spin expectation value). This is why the ordering of the red and green circles switches at the CT, i.e., there is a smooth evolution of $A^{\text{eff}}$, which is directly proportional to $\gamma_e^{\text{eff}}$, such that it switches sign at the CT. Remarkably, this implies that the effective dipolar coupling to protons vanishes completely at the CT; hence the ESE modulation also vanishes there, as does the electron-nuclear spin-spin decoherence, leading to the divergence in $T_m$ ($= 8.43(6) \mu s$ at the CT). Meanwhile, the modulation depth grows in proportion to $A^{\text{eff}}$ upon moving away from the CT, as does the electron-nuclear spin-spin decoherence ($T_m \sim 1 \mu s$ far from the CT).

3 Theory and Simulation

Model To further our understanding of ESEEM, particularly the vanishing of hyperfine coupling at the CT, we construct a simplified model with a central spin coupled to a proton spin bath. In order to preserve computational resources for the bath, we model the HoW$_{10}$ complex as an $S = 1$ spin with longitudinal and transverse anisotropy (Fig. 1).

$$\hat{H}_S = D[\hat{S}_z^2 - \frac{1}{3}S(S + 1)] + E(\hat{S}_x^2 - \hat{S}_y^2) + \gamma_e(B_0 - B_{\text{min}})\hat{S}_z,$$

(1)

where $\hat{S}_i$ are spin-1 generators of rotation about axis $i$, while $D$ and $E$ are the 2nd order axial and rhombic anisotropy parameters, respectively. $B_{\text{min}}$ is introduced to shift the CT away from $B_0 = 0$, mimicking the effect of the on-site hyperfine interaction between the Ho electron and nuclear spins; note that this field does not act on the proton bath. The eigenvectors of Eq. (1) at the CT (i.e., $B_0 = B_{\text{min}}$) are $|\pm\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle \pm |\downarrow\rangle)$ and $|0\rangle$, with energies $-\frac{1}{3}|D| \pm E$ and $+\frac{2}{3}|D|$, respectively.
respectively. Here, \(|\uparrow\rangle|, |\downarrow\rangle|\), and \(|0\rangle|\) are the states with \(\langle \hat{S}_z \rangle = \pm 1\) and \(\langle \hat{S}_z \rangle = 0\), respectively. The eigenstates at the CT are singlets, i.e., \(\langle+ |\hat{S}_i|+\rangle = \langle- |\hat{S}_i|-\rangle = \langle0|\hat{S}_i|0\rangle = 0\) for \(i = x, y, z\).

For complete generality, we set \(D = -6\) GHz, \(|E| = 600\) MHz and \(B_{\text{min}} = 10\) mT, i.e., given that the underlying Hamiltonian is different, we make no attempt to match the spectrum to that of HoW\(_{10}\). In the vicinity of \(B_{\text{min}}\), the lowest eigenenergies depend quadratically on \(B_0\). Because \(|\pm\rangle|\) are energetically well-separated from \(|0\rangle|\) we project onto the two-dimensional subspace defined by the former, wherein,

\[
\begin{align*}
\hat{S}_z^2 &\to 1, \quad \hat{S}_z \to \sigma_z, \quad \hat{S}_x^2 - \hat{S}_y^2 \to \sigma_x, \quad \{\hat{S}_x, \hat{S}_y\} \to 2\sigma_y, \\
\hat{S}_x &\to 0, \quad \hat{S}_y \to 0, \quad \{\hat{S}_y, \hat{S}_z\} \to 0, \quad \{\hat{S}_z, \hat{S}_x\} \to 0.
\end{align*}
\]

(2)

The Pauli matrix, \(\sigma_i\), generates rotations around the \(i^{\text{th}}\) axis of the Bloch sphere defined by \(|\pm\rangle|\). Using this notation, the Hamiltonian reduces to \(\hat{H}_S \to E\sigma_z\). According to Eq. (2), rotations over the Bloch sphere are generated by the quadratic transverse anisotropies, \((\hat{S}_x^2 - \hat{S}_y^2)\) and \(\{\hat{S}_x, \hat{S}_y\}\), and an oscillatory magnetic field, \(\vec{B}_1\), polarized along the \(z\)-axis (\(\parallel \vec{B}_0\)). By contrast, in the more common spin-\(\frac{1}{2}\) case, rotations over the Bloch sphere are controlled by \(\vec{B}_1 \perp \vec{B}_0\). This distinction will become important when describing the simulated Hahn-echo sequence below.

The nuclear spin bath, which ultimately causes decoherence and the observed ESEEM effect, is described by \(N\) protons coupled via dipolar interactions to the central \(S = 1\) state,

\[
\hat{H}_{SI} = \hat{S}_z \sum_{m=1}^{N} \left[ A_{sc}^m \hat{I}_z^m + A_{psc}^m (\hat{I}_x^m + \hat{I}_y^m) \right].
\]

(3)

Here, we employ secular \((sc)\) and pseudosecular \((psc)\) approximations with phenomenological
couplings $A_{sc}^m$ and $A_{psc}^m$, respectively. The $\hat{I}_i^m$ are generators that rotate the spin of the $m^{th}$ proton around axis $i$. The protons also undergo their own dynamics, independent of the central spin, according to

$$\hat{H}_I = J \sum_{m \neq n} (\hat{I}_x^m \hat{I}_x^n + \hat{I}_y^m \hat{I}_y^n + \hat{I}_z^m \hat{I}_z^n) + \gamma_H B_0 \sum_{m=1}^N \hat{I}_z^m. \quad (4)$$

That is, each proton in the bath undergoes Larmor precession with a bare frequency $\gamma_H B_0$, and is coupled by a Heisenberg-like interaction to each of the other protons with coupling strength $J$.

To simulate the ESEEM, we numerically recreate the two-pulse Hahn echo sequence in silico by performing a time evolution according to the total Hamiltonian of the system, $\hat{H}_{tot} = \hat{H}_S + \hat{H}_{SI} + \hat{H}_I$. First, we initialize the central spin into an equally weighted superposition of the low energy states, $|\psi(0)\rangle = |+\rangle + |-\rangle$, which simulates a $\pi/2$-pulse. Meanwhile, the nuclear spin bath is initialized into a random, correlated wavefunction. The system is then allowed to evolve for a time interval $\tau$ according to $\hat{H}_{tot}$, whereupon a $\pi$-pulse is applied and the system evolves for a second interval, $\tau$. The off-diagonal matrix element of the density matrix, $\langle + | Tr(\hat{I}_\rho) | - \rangle$, is then extracted, with the trace taken over the nuclear states. As discussed above, the low energy $|\pm\rangle$ eigenvectors at the CT are not the usual $|\uparrow\rangle$ and $|\downarrow\rangle$ states relevant to the $S = \frac{1}{2}$ case. One must therefore take care in applying an appropriate $\pi$-pulse in order to generate an echo. Upon projection onto $|\pm\rangle$ according to Eq. (2), $\hat{H}_S$ and $\hat{H}_{SI}$ are proportional to $\sigma_z$ and $\sigma_x$, respectively. In order for the central spin to refocus, the system must effectively run in reverse, which forces the $\pi$-pulse to take the form $\exp[i\pi \{\hat{S}_x, \hat{S}_y\}/2]$ so that $\hat{H}_S \rightarrow -\hat{H}_S$ and $\hat{H}_{SI} \rightarrow -\hat{H}_{SI}$. That is, in the absence of dynamics of the nuclear spin bath, i.e., $J = \gamma_H = 0$, the central spin completely refocuses so that $|\psi(0)\rangle = |\psi(2\tau)\rangle$. 

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**Coherent ESEEM** As a warm up to our full analysis, we first consider the simple case of a single proton \((N = 1)\) coupled to the central \(S = 1\) spin, with \(A = A_{sc} = A_{psc} = 0.3\) MHz. Fig. 3 displays FFTs of the Hahn echo simulations for several values of \(\tau\) (lower inset displays a representative time trace). In analogy with the \(S = \frac{1}{2}\) case, we associate the lowest frequency FFT peak, and the splitting of the peaks either side of \(\nu_H\), with the effective hyperfine interaction strength, \(A_{\text{eff}}\); the upper inset to Fig. 3 plots this frequency as a function of \(B_0 - B_{\text{min}}\). As can clearly be seen, and in analogy with the experiments, \(A_{\text{eff}} \to 0\) at the CT; indeed, the modulation (not shown) is also zero at the CT. Moreover, far from the CT, such that \(\gamma_e|B - B_{\text{min}}| \gg |E|/\hbar\), \(A_{\text{eff}} \to 2A\); the factor of two in this case is due to renormalization because \(S = 1\) as opposed to \(\frac{1}{2}\). Thus, in the high-field limit, FFT peaks occur at \(2A, \nu_H \pm A\) and \(2\nu_H\). Superimposed on the data in the upper inset to Fig. 3 is a fit to a phenomenological model that assumes \(A_{\text{eff}} \propto \gamma_{e\text{eff}}\), which can be deduced from \(df/dB_0\) via Eq. (1) (see also Fig. 1). This confirms the idea that the variation in \(\gamma_{e\text{eff}}\) (or \(\langle \hat{S}_z \rangle\)) in the vicinity the CT governs the dipolar coupling of the central spin to nearby protons. The final thing to note from these simulations is the absence of decoherence, i.e., the peak echo amplitude does not decay. This is because the two-spin system executes perfectly coherent spin dynamics, with no quantum phase leakage, i.e., there is no bath associated with this model.

**Decoherence** In order to better capture the physics associated with the spin bath, we extend the model to include \(N = 7\) nuclear spins according to Eqs. (3) and (4) [Fig. 4(a)]. This enables simulations on reasonable timescales whilst also capturing the emergence of decoherence. To make the bath more realistic, the individual hyperfine coupling strengths, \(A_i = A_{sc}^i = A_{psc}^i (i = 1\) to \(N)\), are evenly distributed about the average, \(\bar{A}\), such that \(A_i = (1 + \frac{i-4}{10}) \times \bar{A}\). Time traces for
several detunings, $B_0 - B_{\text{min}}$, either side of the CT are displayed in Fig. 4(b). As can be seen, the simulations capture almost all aspects of the experimental results. Very clear ESEEM are observed in all cases, except at the CT. Moreover, the modulation depth increases upon increasing the detuning. The time traces even exhibit a very apparent decay in the coherence of the central spin dynamics, with a phase memory time, $T_m$, that clearly diverges at the CT, i.e., the model qualitatively reproduces the decoherence due to a finite/small nuclear spin bath. The one obvious difference is the residual decoherence seen at the CT in the experiments (Fig. 2), which is attributed to spin-lattice relaxation. This is not included in our model, which is why the time trace is absolutely flat for $B_0 = B_{\text{min}}$.

The ESEEM time traces in Fig. 4(b) exhibit highly complex waveforms, with obvious overtones. The absence of noise in the simulations allows for evolution to very long delay times, $\tau$, from which high resolution FFTs may be obtained [Fig. 4(c)]. The FFTs consist of a forest of sharp peaks representing a histogram of the spectral content associated with the coupled dynamics of the central electron spin and the $N = 7$ nuclear spins. However, one clearly sees that the peaks are clustered in certain frequency regions. One may presume that a larger bath would result in smoother histograms, approaching the Gaussian functions (colored lines) superimposed onto the clusters of peaks. Remarkably, a plot of the center frequencies associated with these Gaussians as a function of the detuning, $B_0 - B_{\text{min}}$ [Fig. 4(d)], reveals qualitatively identical behavior to that observed in the experiments, i.e., a pair of peaks at $\nu_H \pm \frac{1}{2} A_{\text{eff}}$ and a higher frequency peak at $\sim 2\nu_H$; the peaks have therefore been color coded in the same way as in Fig. 4(c). Once again, it can be seen that $A_{\text{eff}} \to 0$ at $B_0 = B_{\text{min}}$, and increases with detuning away from the CT.
4 Concluding Remarks

The focus of this study has been on the coupling between a central electron spin qubit and the surrounding nuclear bath. In particular, we demonstrate both experimentally and theoretically that the qubit decouples completely from the bath at a CT. Simulations reveal a divergence in $T_m$ at the CT, whereas the experiments indicate that the coherence is limited there by other factors. The primary culprit is spin-lattice ($T_1$) relaxation. In particular, molecular vibrations that couple directly to the CF parameter(s) responsible for the CT (the avoided crossing—see Fig. 1) may be expected to cause strong spin-lattice relaxation, an effect that is not included at all in our model.

Electron spin-spin interactions have also been omitted from our model. One may expect the secular part of this interaction (i.e., $\hat{S}^i_z\hat{S}^j_z$) to decouple at a CT in exactly the same way that the proton bath decouples in this study, provided that the interaction is not too strong; the only requirement is that the dipolar coupling strength be substantially weaker than the avoided crossing energy, $\Delta$ ($= 2E$ in our model). While one may safely neglect the secular dipolar interaction in the present work because of the vastly different energy scales associated with the CT ($\Delta$) and the proton Zeeman interaction ($\gamma_H B_0$), this is not the case for electron spin-spin interactions. Dipolar coupling within arrays of nominally identical electron qubits will additionally cause decoherence due to flip-flop processes between resonant spins ($\Delta_1 = \Delta_2$) via the secular interaction ($\hat{S}^i_x\hat{S}^j_x + \hat{S}^i_y\hat{S}^j_y$). Correctly modeling this physics is way more challenging, requiring a much larger bath with resonant and non-resonant qubits, due both to disorder (distributions in $\Delta$) and a dynamic distribution of dipolar interactions within the ensemble. Indeed, such a model contains complex...
many-body physics that lies beyond of the realms of the present investigation.

One may anticipate that future quantum logic devices based on molecular spins will feature controllable entangling interactions between individual qubits. This control would also enable mitigation of unintended flip-flop processes. Likewise, quantum sensing applications involving single qubits are immune to this mode of decoherence. However, it is virtually impossible to remove all sources of magnetic noise (particularly protons), whilst maintaining the complete flexibility that molecular design principles allow. The present investigation therefore highlights the importance of CTs for suppressing spin-spin decoherence. Moreover, one may expect these design principles to apply quite generally to any type of CT. In this regard, hyperfine CTs show the most promise due to weaker coupling to molecular deformations.

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**Correspondence**  Correspondence and requests for materials should be addressed to S. H. and H-P. C. (email: shill@magnet.fsu.edu and hping@ufl.edu).

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Figure 1: Zeeman diagram according to the Hamiltonian of Eq. (1), with the parameters given in the main text. An avoided crossing (a CT) between the two lowest lying states (blue curves - see labeling) can be found when $B_0 = B_{\text{min}} = 10 \text{ mT}$. 

\[ \Delta = 2E \]
Figure 2: (a) HoW$_{10}$ ESE decay curves recorded at 9.18 GHz and 5 K as a function of detuning, $B_0 - B_{\text{min}}$; the white dash curve is a fit to a mono-exponential decay, from which the optimum $T_m = 8.43(6) \mu s$ is deduced. (b) FFTs of the decay curves in (a); prominent peaks in the ESEEM spectra are marked with red, green and blue circles. (c) Plot of ESEEM frequencies in (b) versus $B_0$; the dashed lines correspond to harmonics of the proton Larmor frequency, the open circles are colored according to the same scheme as those in (b), and the vertical red line marks the CT.
Figure 3: FFTs of Hahn echo simulations for the simple case of a single proton ($N = 1$) coupled to the central electron spin (see text for employed parameters) for different detunings, $B_0 - B_{\text{min}}$ = +5 mT (a), +20 mT (b) and +50 mT (c); the inset to (b) shows a representative ESE intensity time trace. Several relevant frequencies are labeled in the FFT spectra. The inset to (a) plots $A^{\text{eff}}$ deduced from the first FFT peak versus $B_0 - B_{\text{min}}$; the red curve is a simple fit that assumes $A^{\text{eff}} \propto df/dB_0$ from Fig. 1.
Figure 4: (a) Schematic of a central spin coupled to $N = 7$ nuclear spins. (b) Simulated ESEEM time traces as a function of detuning, $B_0 - B_{\text{min}}$. (c) FFTs of the time traces in (b). (d) Centers of the main FFT peaks in (c) as a function of $B_0$; the circles in (c) and (d) are colored according to the same scheme as Fig. 2.