Quenching spin decoherence in diamond and single-molecule magnets

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Spin relaxation times $T_1$ and $T_2$

- $T_1$: Relaxation from the excited state to the ground state. The total magnetization is changed (Energy-costing process). Typically caused by spin-lattice interactions.

- $T_2$: Phase relaxation of spin precession. The total magnetization is NOT changed (Energy-conserving process). Typically caused by temporal spin-spin interactions (spin flip-flop).

\[ \begin{align*}
|\uparrow\rangle & \quad \text{---} \quad \text{v} \sim \frac{1}{T_2} \quad \text{---} \\
& \quad \uparrow \quad \downarrow \\
|\downarrow\rangle & \quad \text{---} \quad \text{---}
\end{align*} \]
High frequency EPR

- Spin polarization @ 2K
  - 240 GHz: 99.4 %
  - 10 GHz: 12 %

- Spin flip-flops are main decoherence source.

- Spin flip-flop rate $\propto$ # of the up- and down-spin pair

- High polarization suppress spin decoherence
Outline

1. EPR with VDI source (P~30 mW)
   - NV centers in diamond
   - Single-molecule magnets

2. FEL-based pulsed EPR (P~1kW)
Diamond and impurities

- Hardest material
- Excellent thermal conductor
- A diamond is a crystal of tetrahedrally bonded carbon atoms.
- Diamond is classified by impurity contents.

<table>
<thead>
<tr>
<th>Type</th>
<th>Ia</th>
<th>Ib</th>
<th>IIa</th>
<th>IIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural abundance</td>
<td>~98 %</td>
<td>~0.1 %</td>
<td>1~2 %</td>
<td>~0 %</td>
</tr>
<tr>
<td>Nitrogen (ppm)</td>
<td>~2×10^3</td>
<td>1~10^2</td>
<td>~1</td>
<td>~1</td>
</tr>
<tr>
<td>Others (ppm)</td>
<td></td>
<td>1~10^2</td>
<td>~1</td>
<td>~100 (B)</td>
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<tr>
<td>Color</td>
<td>Clear~Yellow</td>
<td>Yellow</td>
<td>Clear</td>
<td>Blue</td>
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</tbody>
</table>
NV centers in Diamond

- Quantum information processing
- Single photon source
- Single spin read-out
- Rapid spin polarization
- Long spin coherence time at room temperature

Decoherence of NV center

- N electron spin flip-flops

- No temperature dependence of $T_2$ @ 10 GHz
Continuous wave EPR

- N (single N) \((S=1/2)\)

\[ H_N = g \mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{\tilde{A}} \cdot \mathbf{I} \]

- \(^{14}\text{N} \ (I=1)\) hyperfine couplings

\[ \Delta E = 240 \text{ GHz} \]
Continuous wave EPR

- $N$ (single $N$) ($S=1/2$)

$$H_N = g \mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$$

- $^{14}N$ ($I=1$) hyperfine couplings
- Signal ratio=1:3:4:3:1

$\Delta E=240$ GHz

$S=1/2$ Nitrogen
Continuous wave EPR

- NV center \((S=1)\)

\[
H_{NV} = g \mu_B B \cdot S + D(S_z^2 + 1/3S(S + 1))
\]

- Zero-field splittings

\[\Delta E = 240 \text{ GHz}\]
Temperature dependence of $T_2$

- Hahn echo sequence

- $T_2$ is obtained by a single exponential fit

- N-V:
  - $T > 11.5 \text{ K} : T_2 = 6.7 \mu s \rightarrow 8.3 \mu s$
  - $T < 2 \text{ K} : T_2 \sim 250 \mu s$

- N:
  - $T > 11.5 \text{ K} : T_2 = 5.5 \mu s \rightarrow 5.8 \mu s$
  - $T = 2.5 \text{ K} : T_2 \sim 80 \mu s$
Quenching spin bath decoherence
• N spin flip-flop process

\[ \frac{1}{T_2} = CP_{\uparrow \downarrow} + \Gamma_{res} = \frac{C}{(1 + e^{T_{z\perp} / T})(1 + e^{-T_{z\perp} / T})} + \Gamma_{res} \]

• 90 % for 10 \times T_2
• 99 % for quenching
• C=0.57 MHz
• \( \frac{1}{\Gamma_{res}} = 250 \) \( \mu s \)
Dipole-dipole interaction

- $C = 0.57 \text{ MHz}$

$$\frac{1}{T_2} \propto P_\uparrow P_\downarrow + \Gamma_{\text{res}} = \frac{C}{(1 + e^{T_{\text{ze}}/T})(1 + e^{-T_{\text{ze}}/T})} + \Gamma_{\text{res}}$$

- Dipole-dipole interaction energy

$$C = \frac{U_d}{h} \approx \left\langle \frac{\mu_0}{4\pi} \frac{\mathbf{m}_1 \cdot \mathbf{m}_2 - 3(\mathbf{n} \cdot \mathbf{m}_1)(\mathbf{n} \cdot \mathbf{m}_2)}{\tilde{d}^3} \right\rangle / h$$

- $\tilde{d} = 2.8 \text{ nm} \rightarrow \text{N contents } \sim 25 \text{ ppm}$

- The sample crystal $= 10 \sim 100 \text{ ppm}$

- $T_2$-based distance measurement (Future plans)
$^{13}$C nuclear spin bath fluctuations

- $1/\Gamma_{\text{res}} = 250 \, \mu$s: Temperature independent relaxation rate

$$
\frac{1}{T_2} \propto \frac{C}{(1 + e^{T_{2e}/T})(1 + e^{-T_{2e}/T})} + \Gamma_{\text{res}}
$$

- Decoherence time caused by $^{13}$C nuclear spin flip-flop process

$$
1/\Gamma_{\text{res}} = 250 \, \mu s
$$

where $\Delta \omega_{nn}$ is NMR linewidth, $N$ is the number of nuclear per volume.


- $T_2 \sim 380 \, \mu$s for $^{13}$C nuclear spin bath fluctuations

Polarizing $^{13}$C nuclear spins

- Suppress fluctuations of $^{13}$C nuclear spin bath to further increase spin decoherence time.

- Dynamic nuclear polarization (DNP) may be able to polarize the nuclear spin bath.

- High polarization of N electron spins is a key.

A. van Rynbach, S. Takahashi, J. van Tol et al., unpublished

$|m_s=\uparrow, m_I=\uparrow > \rightarrow \text{EPR} \rightarrow |m_s=\uparrow, m_I=\downarrow >$

$|m_s=\downarrow, m_I=\uparrow > \rightarrow \text{EPR} \rightarrow |m_s=\downarrow, m_I=\downarrow >$

$T_x << T_1$
We demonstrated that spin decoherence of electron spin bath can be quenched by high-fields and low-temperatures.

We can access a nuclear spin bath decoherence.

Temperature dependence of $T_2$ is potentially useful for distance measurements.
Outline

1. EPR with VDI source (P~30 mW)
   - NV centers in diamond
   - Single-molecule magnets

2. FEL-based pulsed EPR (P~1kW)
Single-molecule magnets

- High-spin molecular magnets made by metal-ion clusters
- Chemically fabricated quantum dots
- \(S=10\) \(Fe_8\) SMM
  \[\text{Total spin} = (6-2) \times 5/2 = 10\]
- Weakly interacts with each other, ensemble properties express themselves as a pseudo-giant single spin.


\[\text{[Fe}_8\text{O}_2\text{(OH)}_{12}(\text{C}_6\text{H}_{15}\text{N}_3)_6\text{Br}_7(\text{H}_2\text{O})\text{Br} \cdot 8\text{H}_2\text{O}}\]
Energy barrier

- Anisotropy due to crystal field.
- For Fe₈, uniaxial anisotropy
- Energy barrier = DS₂ ≈ 30K
- Superparamagnets at high T
- Magnetic relaxation becomes very slow at low T, so becomes magnets.
Quantum ↔ Classical

macroscale
permanent magnets micron particles

nanoscale
nanoparticles clusters Molecular clusters Individual spins

\[ S = 10^{23} \quad 10^{10} \quad 10^8 \quad 10^6 \quad 10^5 \quad 10^4 \quad 10^3 \quad 10^2 \quad 10 \quad 1 \]

**multi-domain**
nucleation, propagation and annihilation of domain walls

**single-domain**
uniform rotation

**magnetic moment**
quantum tunneling, quantum interference

\( \mu_0 H (mT) \quad \mu_0 H (mT) \quad \mu_0 H (T) \)
cw EPR – angle dependence

- Spin Hamiltonian for individual Fe$_8$ SMM
  \[ H = \mu_B g S \cdot B_0 + DS_z^2 + E(S_x^2 - S_y^2) \]
  \( g=2.00, \ D=-6.15 \text{ GHz}, \ E=1.14 \text{ GHz} \)
- A single crystal was rotated as function of a magnetic field.
cw EPR – temperature dependence

- $B \sim$ easy axis
- Indicates the ground state peak at 4.6 T.

$m_s = -10 \leftrightarrow m_s = -9$
High polarization
Spin decoherence of SMMs

- No publication of spin echo from single-crystal SMMs.

- $T_2$ will be very short because of strong fluctuations of SMM spin bath.

- There are some observations of spin echo from highly diluted molecular magnets.
  

- Fluctuations of electron spin bath can also be reduced by polarizing the spin bath.
First spin echo measurement

- Strong temperature dependence indicates electron spin bath fluctuations.

- $T_1 \sim 1 \text{ ms} \gg T_2$

$T_2$ measurement

![Graph showing the relationship between magnetic field and echo area with $T_2 = 712 \pm 15$ ns]
\begin{itemize}
  \item S=10 spin flip-flop process:
  \[
  \frac{1}{T_2} = A \sum_{m_s=-10}^{9} W(m_s) P_{m_s} P_{m_s+1} + \Gamma_{\text{res}}
  \]
  
  \[
  P_{m_s} = \frac{e^{-\beta E(m_s)}}{Z}
  \]
  
  \[
  W(m_s) = \left| \langle m_s + 1, m_s | S_1^+ S_2^- | m_s, m_s + 1 \rangle \right|^2
  \]
  
  \[
  + \left| \langle m_s, m_s + 1 | S_1^- S_2^+ | m_s + 1, m_s \rangle \right|^2
  \]

  \item Spin decoherence is significantly suppressed by spin polarization.

  \item \( \Gamma_{\text{res}} \) may be caused by couplings to nuclear moments (Proton & \(^{57}\)Fe) and phonon.

\end{itemize}

No $^1$H spin bath decoherence?

- Deuterated Fe$_8$ SMM was recently studied.
- Deuterium has much smaller magnetic moments than Hydrogen.
- Temperature dependence of $T_2$ is about same.
- A theory predicts that phonon decoherence $>>$ nuclear decoherence.

**$T_1$ relaxation time**

- Two decay curves have been measured.

- $T_{\text{long}}$: temperature-dependent ($T_1$)

- $T_{\text{short}}$: temperature-independent (Spectral diffusion?)

- Other $T_1$ measurements

  S. Takahashi et al., unpublished.
• We observed spin echo in Fe$_8$ single crystals for the first time by suppressing spin decoherence.

• Low temperature $T_2$ is limited $\sim 1 \mu$s.

• We are investigating the other decoherence sources and the origin of $T_1$. 
Outline

1. EPR with VDI source (P~30 mW)
   - NV centers in diamond
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2. FEL-based pulsed EPR (P~1kW)

Tip angle of spins: $\alpha \propto B_{MW} \cdot t$
High-frequency EPR

- Finer spectral resolution
- Less motional averaging
- Higher spin polarization
- Low-power/High-frequency pulsed EPR spectrometers (>150 GHz)
  - NHMFL (120, 240, 336 GHz)
  - Leiden (275 GHz)
  - Frankfurt (180 GHz)
  - Freie U. Berlin (360 GHz)
  - UCSB (240 GHz)
- High-power/High-frequency (P ~ 100 - 1kW)
- Better time resolution
High-power pulsed EPR

- Short spin relaxation time ($T_1$ and $T_2$), e.g. SMMs & proteins in aqueous solution.

- Fast structure change, e.g. “film” proteins in action

- 10 GHz and 35 GHz pulsed EPR systems with 100 ns time resolution

- High frequency EPR for better time resolution
  - Shorter deadtime ($Q/\omega$)

- A few 95 GHz systems.
  - Freed group (Cornell)
  - Smith group (St. Andrews, UK)

- No commercial high power THz source.

- UCSB FEL covers up to 4.7 THz (1.26 THz = 45 tesla for $g=2$ EPR)

Setup overview

1. Free-electron lasers with injection-locking

- **Cavity dump coupler**
- Injection-locking system

2. Pulse Slicer

- 150 ps Nd:YAG laser (532 nm, 120 mJ EKSPLA)
- For 2nd pulse
- Reflection switch
- Back-to-back corrugated horn

3. EPR spectrometer

- Fabry-Perot cavity
- EPR spectrometer
We built 240 GHz spectrum analyzer to observe FEL spectrum.

UCSB FEL employs a 6 m (20 feet) long Fabry-Perot cavity (25 MHz mode spacing) in the undulator.

Radiation modes of the FEL depend on stochastic start-up process and FEL gain bandwidth ~1 GHz.

Multimode lasing and pulse-to-pulse frequency fluctuations are observed.

1. Start-up

2. Amplification

3. Saturation (Mode beating)
Injection-locking

- Two state-of-the-art instruments
  - VDI tunable ultra-stable injection source (~30 mW)
  - Thomas-Keating isolator
- Si plate coupler
- 240 GHz spectrum analyzer
- 240 GHz isolator (TK)
Single-mode lasing

- No pulse-to-pulse frequency fluctuation
- Sub-MHz linewidth (~500 kHz@2 µs pulse duration)

Pulse slicer

- Pulse slicer is made by photo-activated Si or GaAs switches.
- Rising and falling times are < 150 ps.

- Pulsewidth is varied by a delay line of YAG laser.

New pulse slicer

- Contrast is a key!
- Tune Si wafer thickness
- > 60 dB contrast ratio

![Diagram of pulse slicer system]

YAG laser (532 nm, 120 mJ EKSPLA)
Delay system

Back-to-back corrugated horn

1st pulse

Reflection switch

Transmission switch

2nd pulse

Delay system

YAG laser

Reflection (dB)

wafer 1
wafer 2
wafer 3
wafer 4
wafer 5

Reflection (dB)

Angle (degrees)

Brewster's angle

off
$T_2$-based distance measurement

1. Concentration dependence of nitroxide and spin-labeled lipid vesicles

2. DNP of protons.

3. Assembly of proteorhodopsin

• High-frequency EPR can quench electron spin decoherence with low-temperatures.

• High-frequency EPR can access nuclear spin decoherence.

• FEL-based EPR for ns spin dynamics

• Possible $T_2$-based distance measurement
Acknowledgement

• UCSB - Physics
  – Jerry Ramian
  – David Enyeart
  – Dan Allen
  – Thor Visher
  – Kiyotaka Akabori
  – Melissa Anholm

  – D. D. Awschalom

• Delft UT
  – Ronald Hanson

• NHMFL
  – Johan van Tol

• UCSD
  – David Hendrickson
  – Chris Beedle

• UCSB – Chemistry
  – Songi Han
  – Devin Edwards

• Research funding
  – NSF DMR-0321365
  – NSF DMR-0520481
  – W. M. Keck foundation
Acknowledgement

- NHMFL – Johan van Tol
- UCSD – David Hendrickson – Chris Beedle
- UCSB – Chemistry – Songi Han

December 12th, 2008
Cavity dump coupler

- Amplification of FEL output for sub-ns time resolution.
- Normal FEL coupler has 5~20% coupling, so only 5~20% of intracavity power couples out.
- Cavity dump coupler (CDC) couples out the entire intracavity power.

FEL cavity

S. Takahashi et al., manuscript in preparation (2009).
Isolator

- Huge reflection and tiny sample signal.
- Inputs ~ kW, EPR < nW → ΔP > 120 dB
- 1st isolation: wire-grid polarizer (EPR is circularly polarized.)
- 2nd isolation: Photo-activated Si or GaAs switch
- Short switching ( <100 ps)
Fabry-Perot cavity

- Semi-confocal cavity
- EPR couples to H-field; water couples to E-field
- Aqueous sample is mounted at H-field maximum and E-field minimum.
- Two translation stages
  1. End-mirror positioning
  2. Sample positioning
- *In-situ* T-stage control
- Finesse ($\Delta l/l$) ~ 50
“Bottom-up” approach

Molecular (bottom-up) approach ↔ Classical (top-down) approach