Electron Magnetic Resonance at the MagLab

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Outline of talk:
• What is Electron Magnetic Resonance (EMR)?
• Spin-orbit + crystal field interaction – origin of magnetic anisotropy
• Anisotropic Zeeman interaction ($g$-anisotropy) – examples
• Field-independent magnetic anisotropy – examples
• Molecular clusters, or single-molecule magnets (if time)
• Spin-spin dipolar interactions – structure measurements (if time - unlikely)
What is EMR & Why High Fields

Electron Paramagnetic Resonance (EPR)
A.k.a. Electron Spin Resonance (ESR)
At MagLab: Electron Magnetic Resonance (EMR)
(includes other forms of resonance involving electrons)

Classical point-of-view: Larmor (spin) precession

$$\tau = \hbar \frac{ds}{dt} = m \times B$$

$$\omega_L = \frac{geB}{2m_e}$$

Quantum mechanical point-of-view: Zeeman quantization

For spin $S = \frac{1}{2}$:

$$S_z = m_S \hbar, \quad m_S = \pm \frac{1}{2}$$

$$E = -\vec{m} \cdot \vec{B} = g\mu_B B m_s$$

$$hf = \hbar \omega_L = g\mu_B B$$

Protons: 7.6 MHz/T

For free electron

$$\frac{\omega_L}{2\pi B} = \frac{f_L}{B} = 28 \text{ GHz/T}$$
Electron Paramagnetic Resonance (EPR)
A.k.a. Electron Spin Resonance (ESR)
At MagLab: Electron Magnetic Resonance (EMR)
(includes other forms of resonance involving electrons)

Unpaired electrons are not free
They reside in atomic orbitals and are involved in chemical bonding
They therefore interact with each other and their environment...
...via spin-orbit, spin-spin and electron-nuclear hyperfine interactions

STRUCTURE: lattice or molecular structure
Electron Paramagnetic Resonance (EPR)
A.k.a. Electron Spin Resonance (ESR)
At MagLab: Electron Magnetic Resonance (EMR)

Quantum mechanical point-of-view: Zeeman quantization

For spin $S = \frac{1}{2}$: $S_z = m_S \hbar$, $m_S = \pm \frac{1}{2}$

$$E = -\vec{m} \cdot \vec{B} = g \mu_B B m_s$$

$\Delta m_s = \pm 1$

$hf = \hbar \omega_L = g \mu_B B$

$m_s = +\frac{1}{2}$

$m_s = -\frac{1}{2}$
The EMR Facility in Tallahassee


\[ \hat{H} = \hat{H}_{\text{Zeeman}} + \hat{H}_{\text{Micro}} \]

Energy (cm\(^{-1}\))

Magnetic Field (tesla)

Frequency (GHz)

Commercial instruments

Pulsed

1.00 cm\(^{-1}\)

0.12 meV

30.0 GHz

1.43 K
Molecular Nanomagnetism

- Potential for 100 Tb/in²
- Monodisperse arrays
- Rational design
- Requires strong magnetic anisotropy: combination of crystal field (orbital) and spin-orbit coupling.
- Quantum fluctuations become a major problem.
Consider Spin-Orbit, $\lambda L.S$, Interaction First

Lanthanides: $\lambda L.S \sim 1000s \text{ cm}^{-1}$, $\Delta_{CF} \sim 100 \text{ cm}^{-1}$

Gives rise to a (rigid) total angular momentum quantum number $J$

\[ J = L - S \]

$L = 3$

$S = 1/2$

$J = 5/2$

4f$^1$ Ce(III)
Magnetic Anisotropy
Two interactions, two regimes: (1) $\lambda L . S \gg \Delta_{\text{CF}}$

Consider Spin-Orbit, $\lambda L . S$, Interaction First
Lanthanides: $\lambda L . S \sim 1000\text{s cm}^{-1}$, $\Delta_{\text{CF}} \sim 100 \text{ cm}^{-1}$

Gives rise to a (rigid) total angular momentum quantum number $J$

$$J = L - S$$

$L = 6$

$S = \frac{3}{2}$

$J = \frac{9}{2}$
Magnetic Anisotropy
Two interactions, two regimes: (1) $\lambda L.S >> \Delta_{CF}$

Consider Spin-Orbit, $\lambda L.S$, Interaction First
Lanthanides: $\lambda L.S \sim 1000$ cm$^{-1}$, $\Delta_{CF} \sim 100$ cm$^{-1}$

Gives rise to a (rigid) total angular momentum quantum number $J$

$$J = L - S$$

4$^f^6$ Eu(III)

$L = 3$

$S = 3$

$J = 0$
Magnetic Anisotropy
Two interactions, two regimes: (1) $\lambda L.S >> \Delta_{CF}$

Consider Spin-Orbit, $\lambda L.S$, Interaction First
Lanthanides: $\lambda L.S \sim 1000\text{s cm}^{-1}$, $\Delta_{CF} \sim 100\text{ cm}^{-1}$

Gives rise to a (rigid) total angular momentum quantum number $J$

$J = S$

$L = 0$

$S = \frac{7}{2}$

$J = \frac{7}{2}$
Consider Spin-Orbit, $\lambda L.S$, Interaction First.
Lanthanides: $\lambda L.S \sim 1000 \text{ s cm}^{-1}$, $\Delta_{\text{CF}} \sim 100 \text{ cm}^{-1}$

Gives rise to a (rigid) total angular momentum quantum number $J$

$J = L + S$

$L = 6$

$S = 2$

$J = 8$
Magnetic Anisotropy
Two interactions, two regimes: (1) $\lambda L.S >> \Delta_{\text{CF}}$

Next Consider the Crystal Field Interaction

- Simple-minded electrostatic considerations
- Works because of contracted nature of $4f$ shell
- Quadrupole approximations of $4f$ distributions

Example:


Pc = Phthalocyanine
Magnetic Anisotropy
Two interactions, two regimes: (1) $\lambda L.S \gg \Delta_{CF}$

Quantum Mechanical Picture


$\text{Tb(Pc)}_2^-$

Pc = Phthalocyanine
Magnetic Anisotropy

Two interactions, two regimes: \((2) \Delta_{CF} \gg \lambda L \cdot S\)

3d Transition Metals

Example: \(3d^9\) Cu(II)

\(\Delta_{CF} \sim 10^4 \text{ cm}^{-1}, \lambda \sim 100\text{s cm}^{-1}\)

- Electrostatic approximation
- Covalency changes picture
- Orbital momentum “quenched”

Spin-orbit: 2\(^{nd}\) order perturbation

\[
\hat{H} = \mu_B \vec{B} \cdot \left( g_e \hat{1} + 2 \lambda \vec{\Lambda} \right) \cdot \hat{S}
\]

\[
\Lambda_{ii} = \sum_n \left| \langle \psi_0 | \hat{L}_i | \psi_n \rangle \right|^2 \frac{E_n - E_0}{E_n - E_0}
\]

\[
\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{S}
\]

\(\vec{g} = \) Anisotropic g-tensor

\[
g_{xx,yy} \approx 2 + \frac{2 \lambda}{\Delta_1}; \quad g_{zz} \approx 2 + \frac{8 \lambda}{\Delta_2}
\]
Magnetic Anisotropy

Two interactions, two regimes: $\Delta_{CF} \gg \lambda L \cdot S$

Orbitally degenerate case

Jahn-Teller distortion

Non-degenerate

$S = \frac{1}{2}$

3d Transition Metals

Example: 3d$^9$ Cu(II)

$\vec{L}_{x,y}$

$\Delta_2$

$\Delta_1$

Cavity transmission (arb. units - offset)

$f = 92.5 \text{ GHz}$

Magnetic field (tesla)

$2.057(6)$

$2.307(5)$
EPR Under Pressure: Coordination polymer CuF<sub>2</sub>(pyz)H<sub>2</sub>O<sub>2</sub>

With J. Schlueter (Argonne); J. Manson (EWU); E. Brechin (Edinburgh)

0.1 GPa
Phase I

Magnetic \( d_{x^2-y^2} \) orbital

Prescimone, Schlueter, Hill et al., Angew. Chem. 51, 7490 (2012)
Halder, Schlueter et al., Angew. Chem. Int. Ed. 50, 419 (2011)
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Study of $g$-anisotropy in a powder sample

Effective Spin-Only Hamiltonian with $s = \frac{1}{2}$

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{s}$$

X-band, 9 GHz

$g_x = 2.05$

$g_y = 2.07$

$g_z = 2.35$

Absorption (arb. units)

1st derivative (arb. units)

Magnetic field (tesla)
Study of $g$-anisotropy in a powder sample

Effective Spin-Only Hamiltonian with $s = \frac{1}{2}$

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{s}$$

Q-band, 33 GHz

Absorption (arb. units)

First derivative (arb. units)

Magnetic field (tesla)

$g_z = 2.35$

$g_y = 2.07$

$g_x = 2.05$
Example: a Biological Organic Radical
Very weak spin-orbit coupling requires high-fields


**Carbon/Nitrogen centered radical**

Structural studies of azurin utilizing Tryptophan radicals. This was done at 25T and ~700 GHz and could not be done at lower fields.
Zero-Field Splitting ($S > \frac{1}{2}$)

Effective Spin-Only Hamiltonian

\[ \hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{s} + \lambda \hat{s} \cdot \vec{\Lambda} \cdot \hat{s} \]

Ni$^{II}$ ($3d^8$)
Octahedral

\[ S = 1 \]

EPR Selection rule
\[ \Delta m_S = \pm 1 \]

Spin $S = 1$

Orbitally non-degenerate

e\textsubscript{g}

\textsubscript{t}$_{2g}$

Energy

Magnetic field

\[ m_S = +1 \]

\[ m_S = 0 \]

\[ m_S = -1 \]
Zero-Field Splitting ($S > 1/2$)

Effective Spin-Only Hamiltonian

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{s} + \hat{s} \cdot \vec{D} \cdot \hat{s}$$

In this case, $D = 0$

Degenerate transitions

Ni^{II} (3d^8)
Octahedral

$S = 1$

EPR Selection rule
$\Delta m_s = \pm 1$

$m_s = +1$

$m_s = 0$

$m_s = -1$

Orbitally non-degenerate

$m_s = +1$

Spin $S = 1$
Zero-Field Splitting ($S > \frac{1}{2}$)
Effective Spin-Only Hamiltonian

$$\hat{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \hat{s} + D_{zz} \hat{s}_z^2 + E \left( \hat{s}_x^2 - \hat{s}_y^2 \right)$$

Number of peaks and simulation inform on spin/oxidation state

$D \neq 0$: $2S$ transitions

$D_{zz} = \lambda^2 \Lambda_{zz}$

$m_s = +1$
$m_s = 0$
$m_s = -1$

Spin $S = 1$

EPR Selection rule
$\Delta m_s = \pm 1$

Easy-axis anisotropy
Magnetic bistability (memory)

$E$ term acts as 2nd order perturbation
Mixes $m_s = \pm 1$
Strong quantum fluctuations

$D/g\mu_B$

Magnetic field // $z$