CHEM40111/CHEM40121

Molecular magnetism

4 Magnetic anisotropy

Nick Chilton
G.012 Dover St Building
T: 54584
E: nicholas.chilton@manchester.ac.uk
## Course Overview

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1. Explain the origin of magnetism arising from electrons in atoms and molecules using formal quantum-mechanical terms

2. Compare and contrast the electronic structure of metal ions in molecules and their magnetic properties, for metals across the periodic table

3. Select and apply appropriate models and methods to calculate molecular magnetic properties such as magnetisation, magnetic susceptibility and paramagnetic NMR shift

4. Deconstruct topical examples of molecular magnetism including single-molecule magnetism, molecular quantum information processing and MRI contrast agents
Magnetic anisotropy

- **Definition:**
  - The magnetic properties of a molecule are dependent on the orientation of the applied magnetic field.

- This implies a connection between the magnetic moment and the structure of the molecule.

- Spin angular momentum *does not* directly interact with the environment, but orbital angular momentum *does*.

- If the ground state of a molecule has no orbital angular momentum, the orbital moment is said to be *quenched*. 
Magnetic anisotropy

• However, excited states can influence the ground state

• The spin and orbital moments interact via spin-orbit coupling (SOC)

• Two common effects:
  – The spin ground state can be split in the absence of a magnetic field, zero-field splitting (ZFS)
  – The $g$-value can be anisotropic
Magnetic anisotropy

• Zero-field splitting (ZFS) example:
  – What is the oxidation state of Ni?
  – What is the 3d configuration?
  – What is the ground term?
  – What is the first excited term?
  – Which direction is the unique axis?

• The molecular anisotropy affects the orbital angular momentum of the excited state
  – Influences the ground ‘spin only’ ground state indirectly

• Hamiltonian: \( \hat{H} = D \hat{S}_z^2 \)
The $m_S$ states of the $S = 1$ states are not degenerate in the absence of a magnetic field.

\[ \hat{H} = D \hat{S}_z^2 + \mu_B g B_z \hat{S}_z \]
The $m_S$ states of the $S = 1$ states are not degenerate in the absence of a magnetic field.

Magnetic anisotropy

\[
\hat{H} = D \hat{S}_z^2 + \mu_B g B_x \hat{S}_x
\]
Magnetic anisotropy
Magnetic anisotropy

• This picture is **one** possibility of the ZFS:

\[
|+1\rangle
\]

\[
|0\rangle
\]

\[
|−1\rangle
\]

– Instead of \(|±1\rangle\) being the ground state, it could be \(|0\rangle\)
Magnetic anisotropy

- The magnetic properties of a molecule depend on orientation.

- This implies a connection between the magnetic moment and the structure of the molecule.

- Spin angular momentum does not directly interact with the environment, but orbital angular momentum does.

- If the ground state of a molecule has no orbital angular momentum, the orbital moment is said to be quenched.

- But what if it is not quenched?
The magnetic orbitals of lanthanide ions are the $4f$ orbitals, which are “core-like”

$4f$ orbitals are shielded by the filled $5s$ and $5p$ orbitals which take part in bonding

Therefore the crystal field is much weaker than for $3d$ metals

![Diagram showing the distribution of $4f$, $5s$, and $5p$ orbitals with a stronger peak for $5s$ and $5p$ and a weaker peak for $4f$.]
The 4f orbitals are not appreciably split by the crystal field.
Electrons can hop between orbitals with (nearly) no energy cost – this is orbital degeneracy and gives an orbital angular momentum.

\[ \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \]

\(^6\text{H}\)

Can determine ground term by using Hund’s Rules:

- Place spin-up electrons in \(f\) orbitals from \(m_l = +3\) to \(m_l = -3\)
- If > 7 electrons, place spin-down electrons in \(f\) orbitals from \(m_l = +3\) to \(m_l = -3\)
- Sum up \(m_s\) and \(m_l\) values for all electrons to get total spin \(S\) and total orbital moment \(L\)
Hund’s rules

• Example: dysprosium(III), $4f^9$

$\sum m_s =$

$\sum m_l =$

• $S = 5/2, L = 5 \quad \rightarrow 2S+1L$ ground term \quad $\rightarrow 6H$
Spin-orbit coupling

- The spin and orbital moments influence one another through *spin-orbit coupling*:

\[ \hat{H} = \lambda \hat{L} \cdot \hat{S} \]

\[ \hat{H} = -2J \hat{S}_A \cdot \hat{S}_B \]

(note similarity to exchange Hamiltonian)

- The spin \( S \) and the orbital \( L \) angular momentum can couple in different ways. The *total angular momentum* \( J \) can be:

\[ J = |L - S|, |L - S| + 1, \ldots, L + S - 1, L + S \]

- < 7 electrons: \( J = |L-S| \) ground state
  > 7 electrons: \( J = L+S \) ground state

- Each \( J \) has \( 2J + 1 \) \( m_J \) states:

\[ m_J = -J, -J+1, \ldots, J-1, J \]

Don’t confuse *exchange parameter* and *total angular momentum*
Spin-orbit coupling

- Example: dysprosium(III), $4f^9$
- $S = 5/2$, $L = 5$ (10/2)
- $J = 5/2, 7/2, 9/2, 11/2, 13/2, 15/2$
- 9 $f$ electrons, so $J = 15/2$ ground state

$6H$ \[\text{Spin-Orbit Coupling}\] $6H_{15/2}$

\[\sim 4000 \text{ cm}^{-1}\]
The crystal field has no appreciable effect on the $4f$ orbitals, however it influences the spin-orbit states.

The $J$ states are split into the $m_J$ components in zero-field (see the similarity to ZFS? Different mechanism.)

Dy$^{III}$ has $2J + 1 = 16$ crystal field states split into 8 doublets.

They are doublets due to half-integer $J$ (Kramers theorem)

Crystal field splitting

Usually $< 1000 \text{ cm}^{-1}$
1. Determine the Hamiltonian matrix for $S = 1$ and the Hamiltonian:

$$\hat{H} = D \hat{S}_z^2 + \mu_B g B_x \hat{S}_x$$

given that:

$$\hat{S}_x = \frac{1}{2} (\hat{S}_+ + \hat{S}_-)$$

$$\hat{S}_z |m_s\rangle = m_s |m_s\rangle$$

$$\hat{S}_+ |m_s\rangle = \sqrt{S(S + 1) - m_s(m_s + 1)} |m_s + 1\rangle$$

$$\hat{S}_- |m_s\rangle = \sqrt{S(S + 1) - m_s(m_s - 1)} |m_s - 1\rangle$$