CHEM40111/CHEM40121 Molecular magnetism 4 Magnetic anisotropy



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Course Overview

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 3 Magnetic coupling • Exchange Hamiltonian • Experimental measurements • Vector coupling 	 7 Magnetic resonance imaging Paramagnetic NMR Magnetic resonance imaging Latest research
 4 Magnetic anisotropy 2ero-field splitting Impact on properties Lanthanides Spin-orbit coupling 	 8 Quantum information processing Quantum information DiVincenzo criteria Latest research Question time

Intended learning outcomes

- 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

- <u>Definition</u>:
 - 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*

- 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

- 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.



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



– Instead of $|\pm 1\rangle$ being the ground state, it could be $|0\rangle$

- 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?

Lanthanides

- 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



Lanthanides

• The 4f orbitals are not appreciably split by the crystal field



Lanthanides

• Electrons can hop between orbitals with (nearly) no energy cost – this is orbital degeneracy and gives an *orbital angular momentum*

- 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), 4f⁹



$$\sum m_s =$$

$$\sum m_l =$$

• $S = 5/2, L = 5 \longrightarrow {}^{2S+1}L$ ground term $\longrightarrow {}^{6}H$

Spin-orbit coupling

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

$$\widehat{H} = \lambda \overline{\widehat{L}} \cdot \overline{\widehat{S}} \qquad \qquad \widehat{H} = -2J\overline{\widehat{S}}_A \cdot \overline{\widehat{S}}_B$$

(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:

$$J = |L - S|, |L - S| + 1, ..., L + S - 1, L + S$$

- <7 electrons: J = |L-S| ground state >7 electrons: J = L+S ground state
- Each J has 2J + 1 m_J states: $m_J = -J, -J+1, \dots, J-1, J$

Don't confuse *exchange parameter* and *total angular momentum*

Spin-orbit coupling

- Example: dysprosium(III), 4f⁹
- 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

$$_{6}\text{H}$$
 - Spin-Orbit Coupling



Crystal field splitting

- The crystal field has no appreciable effect on the 4*f* 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 = 16crystal field states split into 8 doublets
- They are doublets due to half-integer *J* (Kramers theorem)



Problem set:

1. Determine the Hamiltonian matrix for S = 1 and the Hamiltonian:

$$\widehat{H} = D\widehat{S}_{z}^{2} + \mu_{B}gB_{x}\widehat{S}_{x}$$

given that:

$$\hat{S}_x = \frac{1}{2} \left(\hat{S}_+ + \hat{S}_- \right)$$
$$\hat{S}_z |m_s\rangle = m_s |m_s\rangle$$
$$\hat{S}_+ |m_s\rangle = \sqrt{S(S+1) - m_s(m_s+1)} |m_s+1\rangle$$
$$\hat{S}_- |m_s\rangle = \sqrt{S(S+1) - m_s(m_s-1)} |m_s-1\rangle$$