CHEM40111/CHEM40121

Molecular magnetism

3 Magnetic coupling

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Course Overview

1 **Fundamentals**	5 **Single-molecule magnets I**
• Motivation • Origins of magnetism • Bulk magnetism	• Single-molecule magnets • Electrostatic model
2 Quantum mechanics of magnetism	**6 Single-molecule magnets II**
• Zeeman effect • Statistical mechanics • Magnetisation • Magnetic susceptibility	• Measuring magnetic relaxation • Relaxation mechanisms • Latest research
3 Magnetic coupling	**7 Magnetic resonance imaging**
• Exchange Hamiltonian • Experimental measurements • Vector coupling	• Paramagnetic NMR • Magnetic resonance imaging • Latest research
4 Magnetic anisotropy	**8 Quantum information processing**
• Zero-field splitting • Impact on properties • Lanthanides • Spin-orbit coupling	• 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

Magnetic coupling

- Magnetic interactions between spins arise from:
  - Direct exchange (overlap of magnetic orbitals)
  - Superexchange (interaction through non-magnetic atoms)
  - Dipolar interactions (through space)

- Generally, we just consider the total exchange interaction

- Example: a dimer of two $S = 1/2$ ions

$$\hat{H} = -2J\hat{\vec{S}}_A \cdot \hat{\vec{S}}_B$$

$$\left|m_{S_A}, m_{S_B}\right\rangle \in \left\{ \begin{matrix} \overset{\downarrow \quad \downarrow}{|-1/2, -1/2\rangle}, \overset{\downarrow \quad \uparrow}{|-1/2, +1/2\rangle}, \\ \underset{\uparrow \quad \downarrow}{|+1/2, -1/2\rangle}, \underset{\uparrow \quad \uparrow}{|+1/2, +1/2\rangle} \end{matrix} \right\}$$

Magnetic coupling

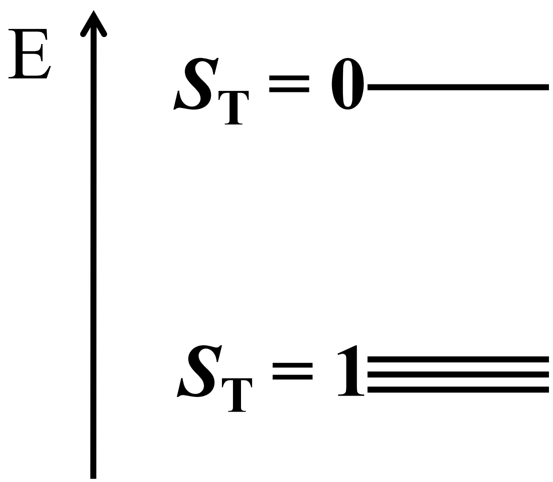
$$
\begin{array}{c} \\ \left\langle -\frac{1}{2},-\frac{1}{2}\right| \\ \left\langle -\frac{1}{2},+\frac{1}{2}\right| \\ \left\langle +\frac{1}{2},-\frac{1}{2}\right| \\ \left\langle +\frac{1}{2},+\frac{1}{2}\right| \end{array}
\begin{array}{c}
\begin{array}{cccc} \left|-\frac{1}{2},-\frac{1}{2}\right\rangle & \left|-\frac{1}{2},+\frac{1}{2}\right\rangle & \left|+\frac{1}{2},-\frac{1}{2}\right\rangle & \left|+\frac{1}{2},+\frac{1}{2}\right\rangle \end{array} \\
\begin{bmatrix}
\left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},+\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},+\frac{1}{2}\right\rangle \\
\left\langle -\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},+\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},+\frac{1}{2}\right\rangle \\
\left\langle +\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},+\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},+\frac{1}{2}\right\rangle \\
\left\langle +\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},+\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2},+\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2},+\frac{1}{2}\right\rangle
\end{bmatrix}
\end{array}
$$

- So what are the matrix elements of the magnetic exchange?

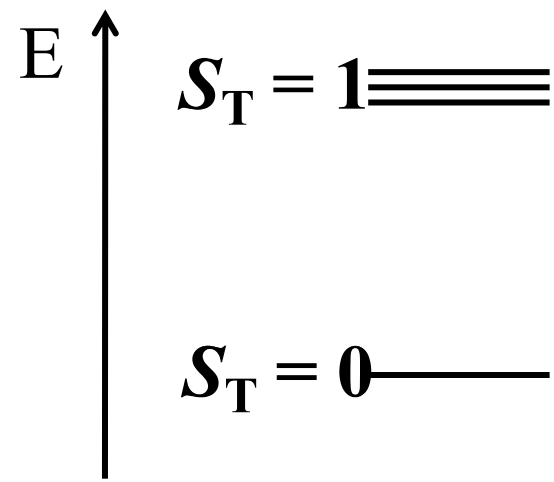
$$-2J\left\langle m_{s_A}', m_{s_B}' \middle| \hat{\vec{S}}_A \cdot \hat{\vec{S}}_B \middle| m_{s_A}, m_{s_B} \right\rangle$$

Magnetic coupling

- Example: two $S = 1/2$ ions



If S_A+S_B is ground state, interaction is ferromagnetic

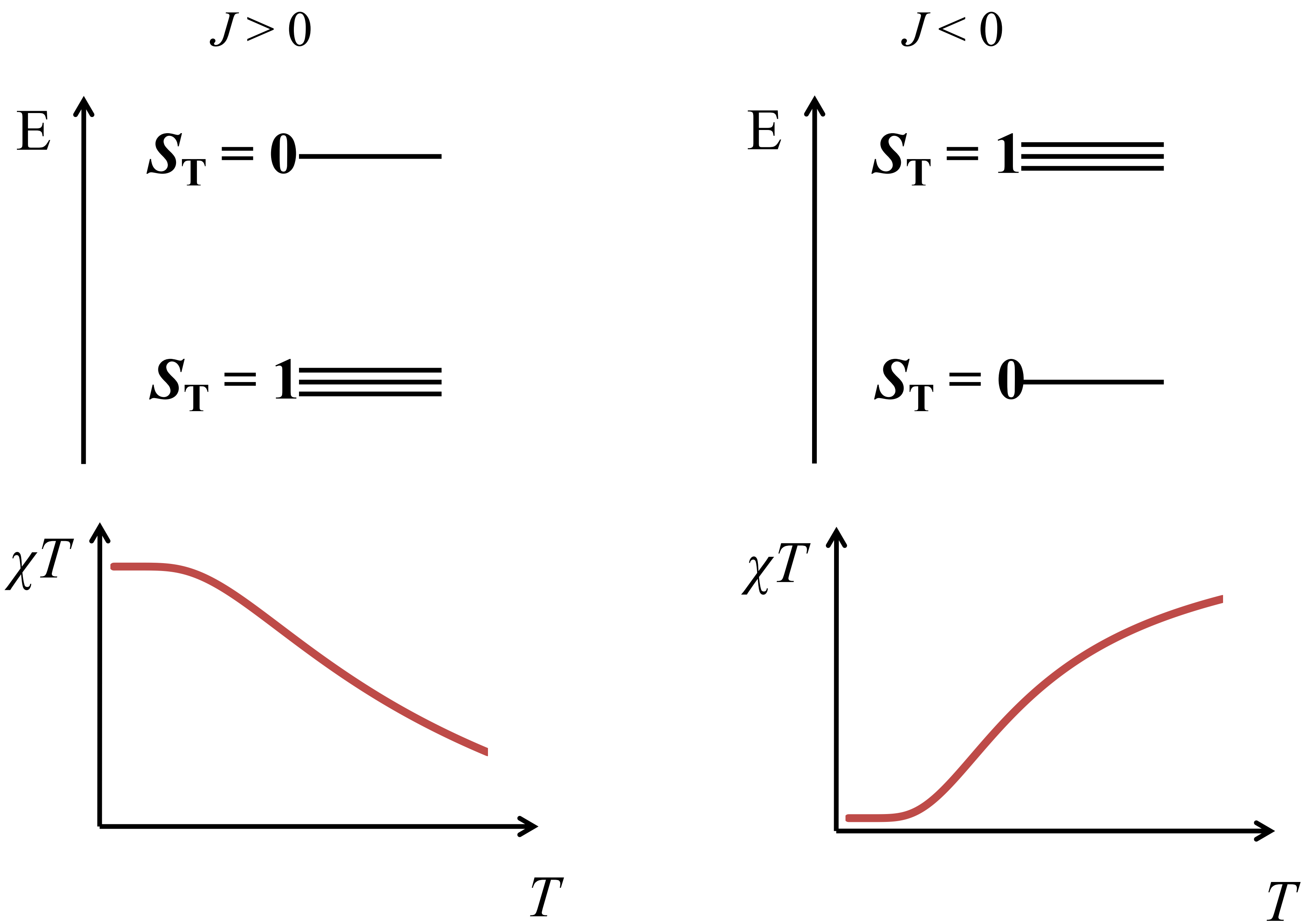


If $|S_A-S_B|$ is ground state, interaction is antiferromagnetic

- For either interaction, *both states exist*

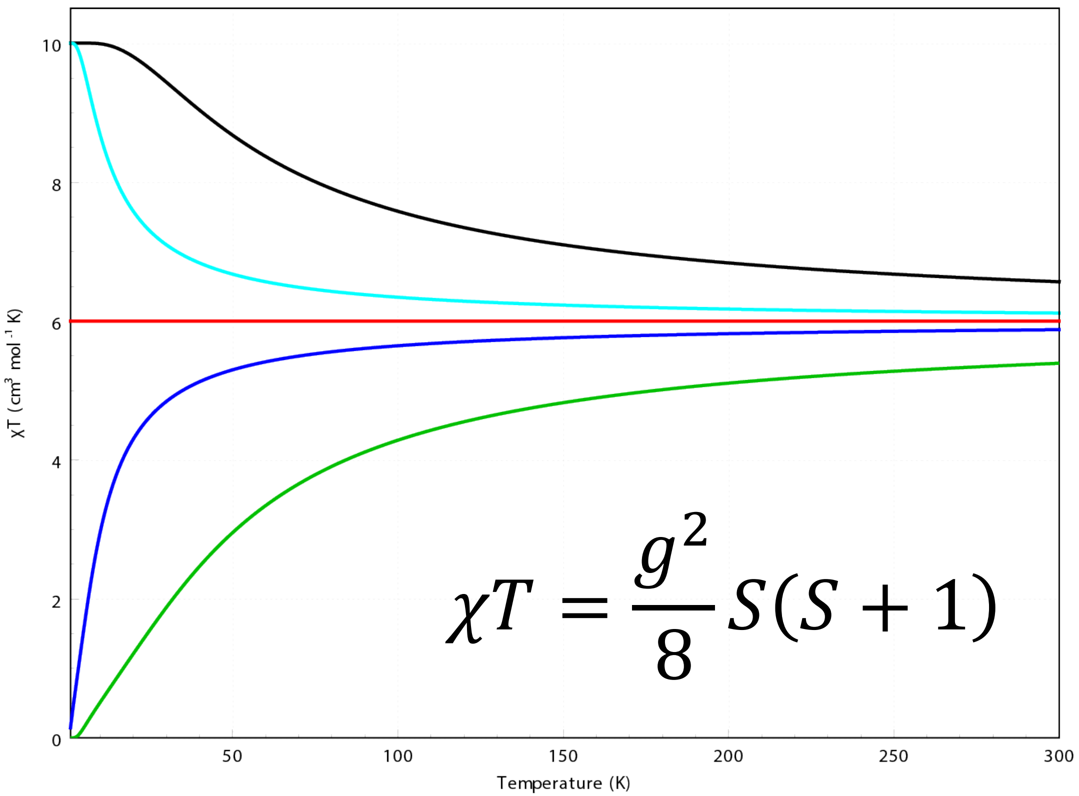
- The strength of the interaction determines the energy between the different states

Magnetic coupling



Magnetic coupling

- We can use the temperature dependence of the magnetic susceptibility to measure the strength of the exchange

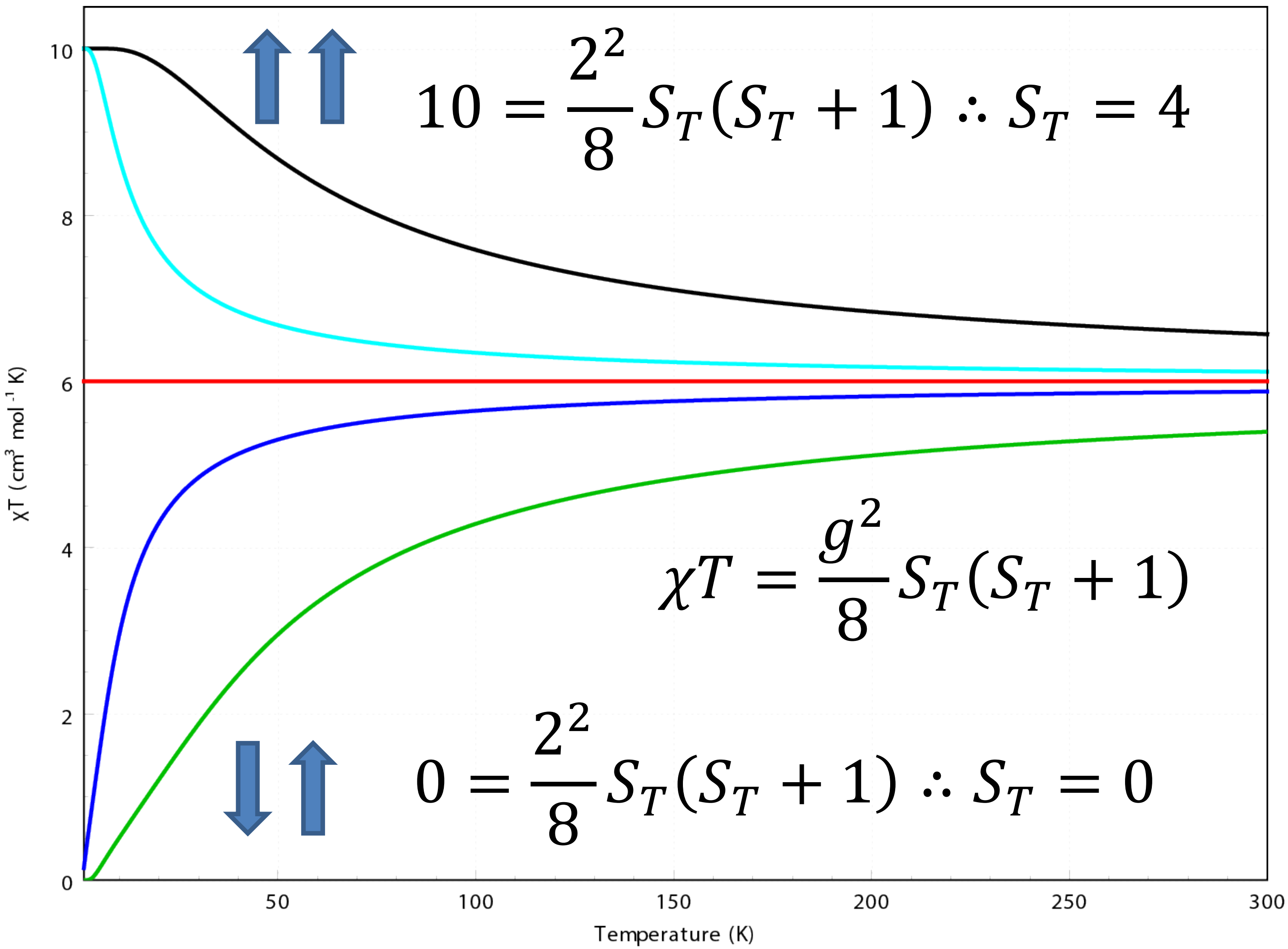


$$\chi T = \frac{g^2}{8} S(S+1)$$

- If χT rises → ferromagnetic ground state
- If χT falls → antiferromagnetic ground state

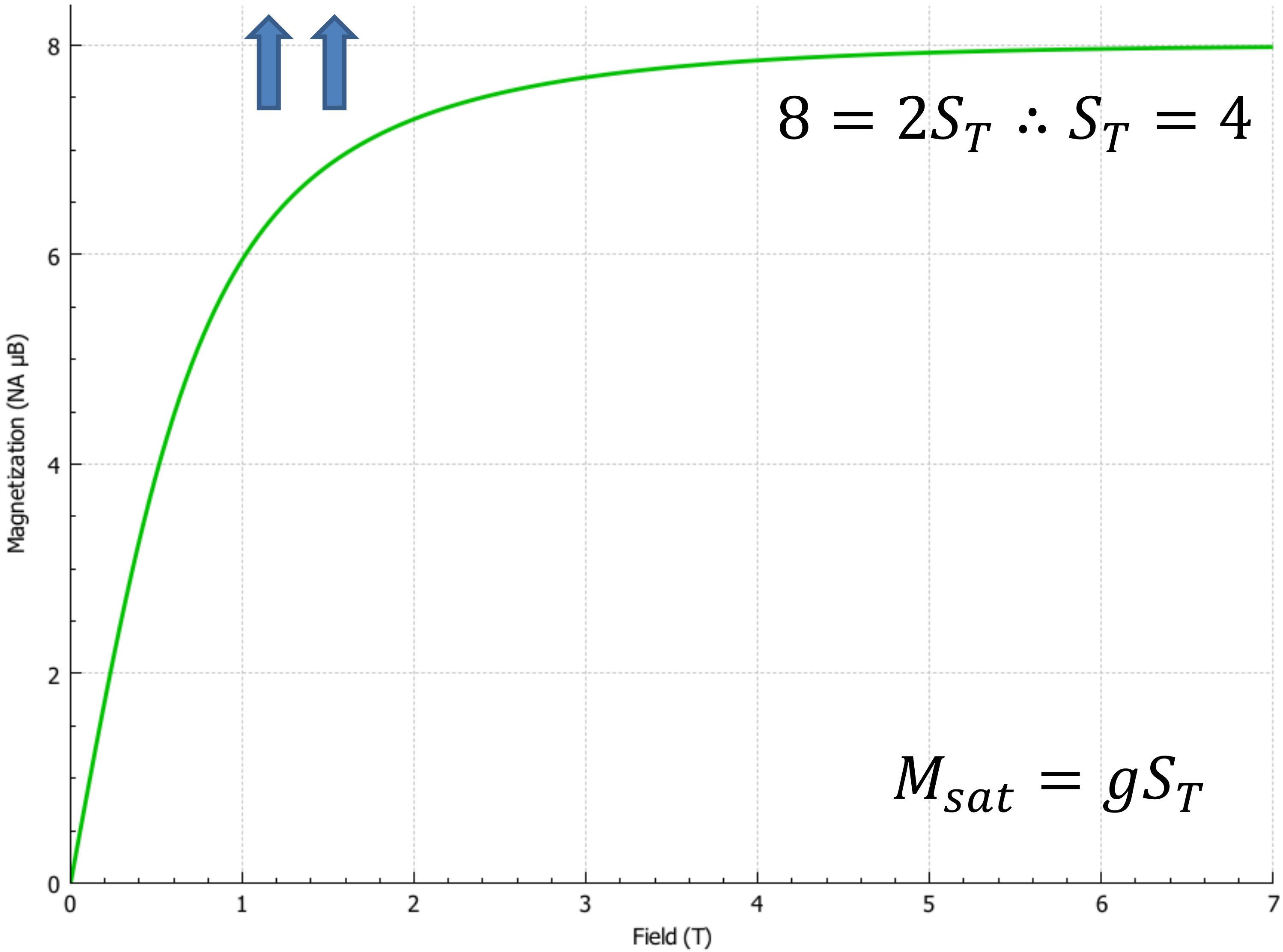
Magnetic coupling

- At low temperatures, χT can reveal ground spin state



Magnetic coupling

- At low temperatures and high fields, *M* also gives ground state

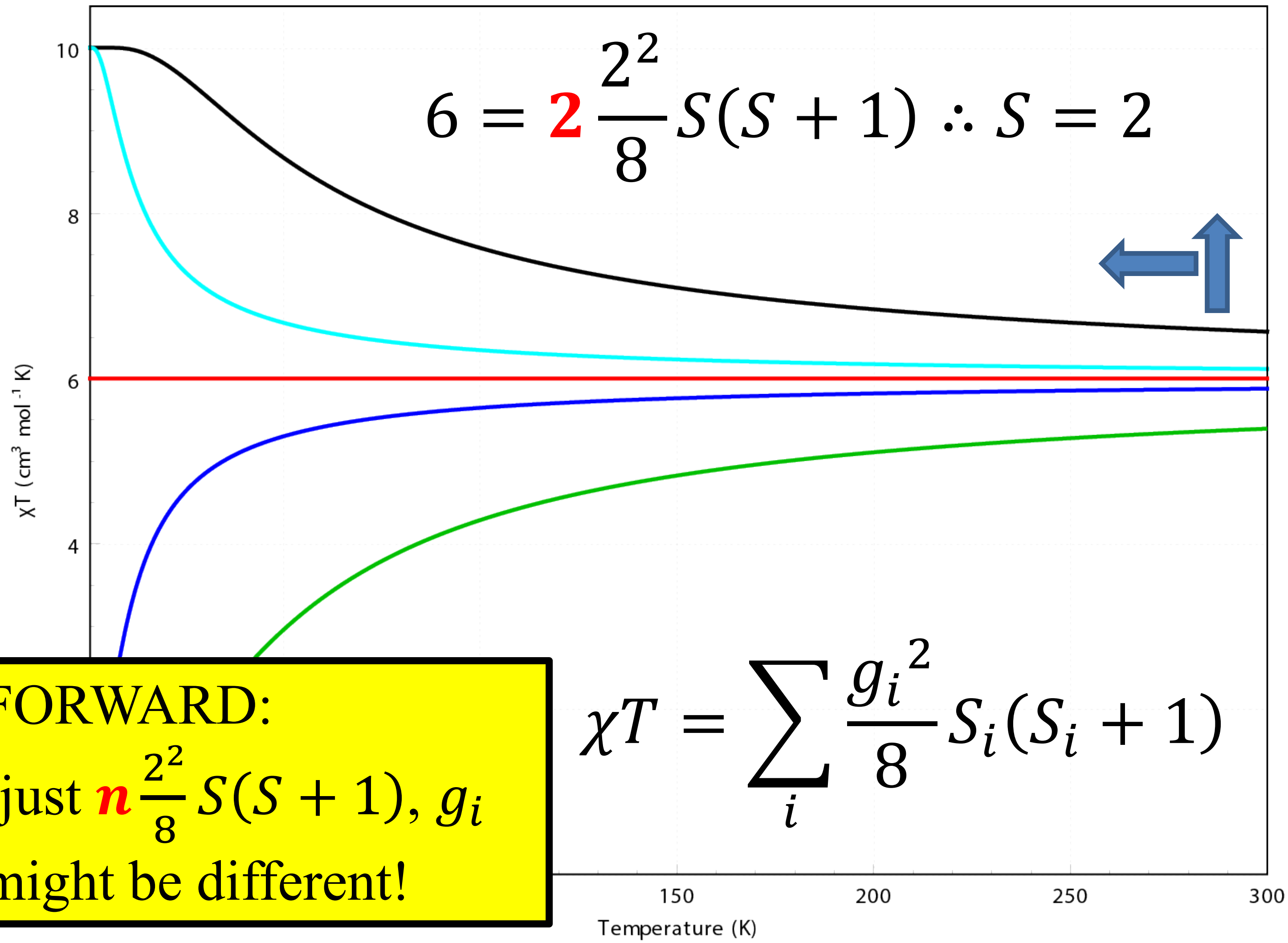


$$8 = 2S_T \therefore S_T = 4$$

$$M_{sat} = gS_T$$

Magnetic coupling

- At high temperatures, χT approaches 'uncoupled' value
  - Not really uncoupled! The ***sum of the Curie contributions of each spin***



$$6 = \mathbf{2}\frac{2^2}{8}S(S+1) \therefore S = 2$$

$$\chi T = \sum_i \frac{{g_i}^2}{8} S_i(S_i+1)$$

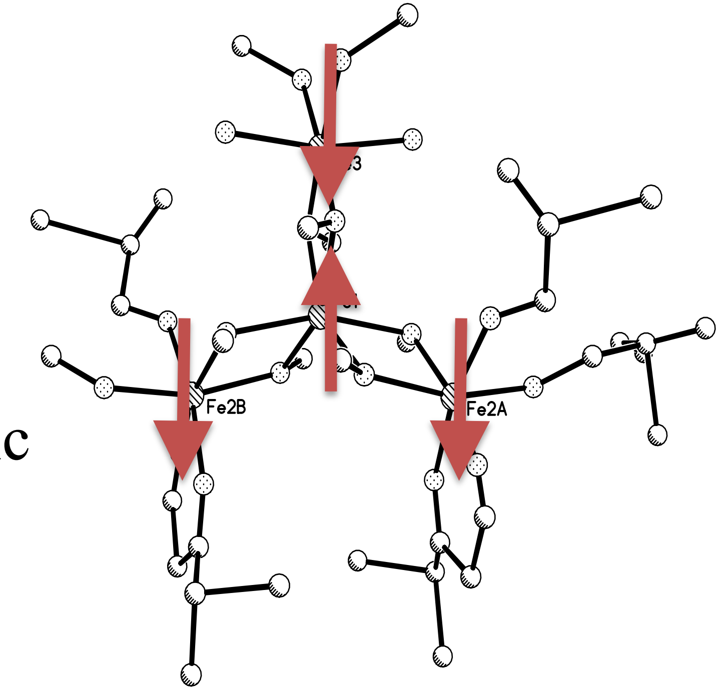
FEED FORWARD:

It's not just $\boldsymbol{n}\frac{2^2}{8}S(S+1)$, g_i and S_i might be different!

Magnetic coupling

- In simple cases, the ground spin state of a molecule S_T can be easily determined by *vector coupling*

- Example: Fe_4 star
  - Fe(III), d^5
  - Octahedral, $S = 5/2$
  - Nearest neighbour antiferromagnetic exchange
  - $S_T = 3\times(5/2) - 5/2 = 5$



  - What is the high temperature limit of χT?
  - What is the low temperature limit of χT?
  - What is the high field, low temperature limit of M?

FEED FORWARD: Don't forget units!!

Problem set:

- Example: Mn_6 ring (symmetric)
  - If the high temperature limit of χT = 18 cm^3 mol^{-1} K
  - And the low temperature limit of χT = 78 cm^3 mol^{-1} K
  - And the high field, low temperature limit of M = 24 N_A μ_B

  - Is the nearest neighbour exchange anti- or ferromagnetic?
  - What is the spin ground state of the molecule, S_T?
  - What are the Mn spins, S_{Mn}?
  - What is a possible oxidation state and geometry for Mn?