CHEM40111/CHEM40121

Molecular magnetism

2 Quantum mechanics of magnetism

Nick Chilton

G.012 Dover St Building

T: 54584

E: nicholas.chilton@manchester.ac.uk

MANCHESTER 1824

The University of Manchester

Course Overview

1 Fundamentals
- Motivation
- Origins of magnetism
- Bulk magnetism

2 Quantum mechanics of magnetism
- Zeeman effect
- Statistical mechanics
- Magnetisation
- Magnetic susceptibility

3 Magnetic coupling
- Exchange Hamiltonian
- Experimental measurements
- Vector coupling

4 Magnetic anisotropy
- Zero-field splitting
- Impact on properties
- Lanthanides
- Spin-orbit coupling

5 Single-molecule magnets I
- Single-molecule magnets
- Electrostatic model

6 Single-molecule magnets II
- Measuring magnetic relaxation
- Relaxation mechanisms
- Latest research

7 Magnetic resonance imaging
- Paramagnetic NMR
- Magnetic resonance imaging
- Latest research

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

Spin states

- Metal ions in octahedral geometry can have multiple unpaired electrons
  - These "add up" to give total spin > s = 1/2:

Ion	Ground state	Spin
Cu(II) d^9	^2E	$S = 1/2$
Ni(II) d^8	^3A	$S = 1$
Cr(III) d^3	^4A	$S = 3/2$
Mn(II) d^4	^5E	$S = 2$
Fe(III) d^5	^6A	$S = 5/2$

- A spin state S has $2S+1$ m_S components:
  - $m_S = -S, -S+1, \ldots, S-1, S$
  - *e.g.* $S = 1$; $m_S = -1, 0, +1$

Zeeman effect

- A magnetic field will cause magnetic moments to align

- In other words, moments anti-parallel to the magnetic field are in a higher energy state than those parallel to the field

- Zeeman Hamiltonian:

$$\hat{H} = \mu_B g \vec{B} \cdot \vec{\hat{S}} = \mu_B g \left(B_x \hat{S}_x + B_y \hat{S}_y + B_z \hat{S}_z \right)$$

- Example:
  - $S = 5/2$, $B_x = B_y = 0$

$$\hat{H} = \mu_B g B_z \hat{S}_z$$

  - What are the energies of the m_S states?

Recap: Solving the Schrödinger equation

- Determine the Hamiltonian matrix $\bar{\bar{\hat{H}}}$
- Diagonalise $\bar{\bar{\hat{H}}}$ (this finds the matrix P such that $P^{-1}\bar{\bar{\hat{H}}}P = D$, where D is a diagonal matrix):

$$D = \begin{bmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_N \end{bmatrix}$$

- The columns of P are the ***eigenvectors*** (wavefunctions), and the diagonal elements of D are the ***eigenvalues*** (energies)

$$P = \begin{bmatrix} C_{i,1} & C_{k,1} & \cdots & C_{N,1} \\ C_{i,2} & C_{k,2} & \cdots & C_{N,2} \\ \vdots & \vdots & \ddots & \vdots \\ C_{i,N} & C_{k,N} & \cdots & C_{N,N} \end{bmatrix}$$

$$|\Psi_i\rangle \quad |\Psi_k\rangle \quad \cdots \quad |\Psi_N\rangle$$

- ***Solution to Schrödinger!***

Recap: Matrix elements

- For a single spin S, the rules are:

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

- m_S is sometimes called S_z
- It is the ***projection*** of S on the z-axis
- $|m_s\rangle$ is an eigenstates of $\hat{S}_z$

Not eigenstates of $\hat{S}_{\pm}$!

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

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

Example: $S = 5/2,\ B_x = B_y = 0$

$$
\begin{array}{c}
\\
\left\langle -\frac{5}{2}\right| \\
\left\langle -\frac{3}{2}\right| \\
\left\langle -\frac{1}{2}\right| \\
\left\langle +\frac{1}{2}\right| \\
\left\langle +\frac{3}{2}\right| \\
\left\langle +\frac{5}{2}\right|
\end{array}
\begin{array}{c}
\begin{array}{cccccc}
\left| -\frac{5}{2}\right\rangle & \left| -\frac{3}{2}\right\rangle & \left| -\frac{1}{2}\right\rangle & \left| +\frac{1}{2}\right\rangle & \left| +\frac{3}{2}\right\rangle & \left| +\frac{5}{2}\right\rangle
\end{array} \\
\begin{bmatrix}
\left\langle -\frac{5}{2}\middle|\hat{H}\middle|-\frac{5}{2}\right\rangle & \left\langle -\frac{5}{2}\middle|\hat{H}\middle|-\frac{3}{2}\right\rangle & \left\langle +\frac{5}{2}\middle|\hat{H}\middle|-\frac{1}{2}\right\rangle & \left\langle -\frac{5}{2}\middle|\hat{H}\middle|+\frac{1}{2}\right\rangle & \left\langle -\frac{5}{2}\middle|\hat{H}\middle|+\frac{3}{2}\right\rangle & \left\langle -\frac{5}{2}\middle|\hat{H}\middle|+\frac{5}{2}\right\rangle \\
\left\langle -\frac{3}{2}\middle|\hat{H}\middle|-\frac{5}{2}\right\rangle & \left\langle -\frac{3}{2}\middle|\hat{H}\middle|-\frac{3}{2}\right\rangle & \left\langle +\frac{5}{2}\middle|\hat{H}\middle|-\frac{1}{2}\right\rangle & \left\langle -\frac{3}{2}\middle|\hat{H}\middle|+\frac{1}{2}\right\rangle & \left\langle -\frac{3}{2}\middle|\hat{H}\middle|+\frac{3}{2}\right\rangle & \left\langle -\frac{3}{2}\middle|\hat{H}\middle|+\frac{5}{2}\right\rangle \\
\left\langle -\frac{1}{2}\middle|\hat{H}\middle|-\frac{5}{2}\right\rangle & \left\langle -\frac{1}{2}\middle|\hat{H}\middle|-\frac{3}{2}\right\rangle & \left\langle +\frac{5}{2}\middle|\hat{H}\middle|-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2}\middle|\hat{H}\middle|+\frac{3}{2}\right\rangle & \left\langle -\frac{1}{2}\middle|\hat{H}\middle|+\frac{5}{2}\right\rangle \\
\left\langle +\frac{1}{2}\middle|\hat{H}\middle|-\frac{5}{2}\right\rangle & \left\langle +\frac{1}{2}\middle|\hat{H}\middle|-\frac{3}{2}\right\rangle & \left\langle +\frac{5}{2}\middle|\hat{H}\middle|-\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2}\middle|\hat{H}\middle|+\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2}\middle|\hat{H}\middle|+\frac{3}{2}\right\rangle & \left\langle +\frac{1}{2}\middle|\hat{H}\middle|+\frac{5}{2}\right\rangle \\
\left\langle +\frac{3}{2}\middle|\hat{H}\middle|-\frac{5}{2}\right\rangle & \left\langle +\frac{3}{2}\middle|\hat{H}\middle|-\frac{3}{2}\right\rangle & \left\langle +\frac{5}{2}\middle|\hat{H}\middle|-\frac{1}{2}\right\rangle & \left\langle +\frac{3}{2}\middle|\hat{H}\middle|+\frac{1}{2}\right\rangle & \left\langle +\frac{3}{2}\middle|\hat{H}\middle|+\frac{3}{2}\right\rangle & \left\langle +\frac{3}{2}\middle|\hat{H}\middle|+\frac{5}{2}\right\rangle \\
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\end{bmatrix}
\end{array}
$$

- So what are the matrix elements?

$$\langle m_S{}' | \mu_B g B_z \hat{S}_z | m_s \rangle = \mu_B g B_z \langle m_S{}' | \hat{S}_z | m_s \rangle = \mu_B g B_z m_s \delta_{m_S{}', m_S}$$

Example: $S = 5/2$, $B_x = B_y = 0$

$$
\begin{array}{c|cccccc}
 & \left|-\frac{5}{2}\right\rangle & \left|-\frac{3}{2}\right\rangle & \left|-\frac{1}{2}\right\rangle & \left|+\frac{1}{2}\right\rangle & \left|+\frac{3}{2}\right\rangle & \left|+\frac{5}{2}\right\rangle \\
\hline
\left\langle-\frac{5}{2}\right| & -\frac{5}{2}\mu_B g B_z & 0 & 0 & 0 & 0 & 0 \\
\left\langle-\frac{3}{2}\right| & 0 & -\frac{3}{2}\mu_B g B_z & 0 & 0 & 0 & 0 \\
\left\langle-\frac{1}{2}\right| & 0 & 0 & -\frac{1}{2}\mu_B g B_z & 0 & 0 & 0 \\
\left\langle+\frac{1}{2}\right| & 0 & 0 & 0 & +\frac{1}{2}\mu_B g B_z & 0 & 0 \\
\left\langle+\frac{3}{2}\right| & 0 & 0 & 0 & 0 & +\frac{3}{2}\mu_B g B_z & 0 \\
\left\langle+\frac{5}{2}\right| & 0 & 0 & 0 & 0 & 0 & +\frac{5}{2}\mu_B g B_z
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$$

- So what are the matrix elements?

$$\langle m_S' | \mu_B g B_z \hat{S}_z | m_s \rangle = \mu_B g B_z \langle m_S' | \hat{S}_z | m_s \rangle = \mu_B g B_z m_s \delta_{m_S', m_S}$$

Zeeman effect

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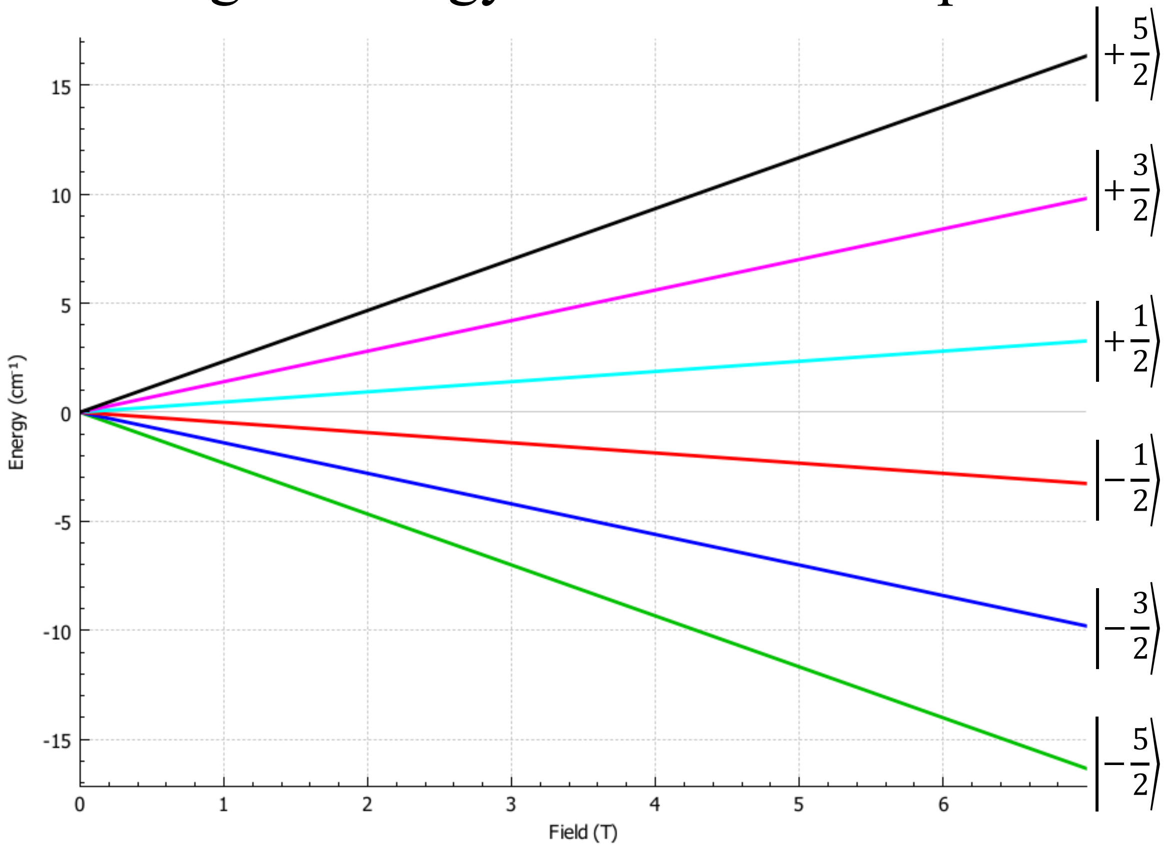
- In other words, moments anti-parallel to the magnetic field are in a higher energy state than those parallel to the field



$$E_{m_S} = \mu_B g m_S B$$

Gradient given by

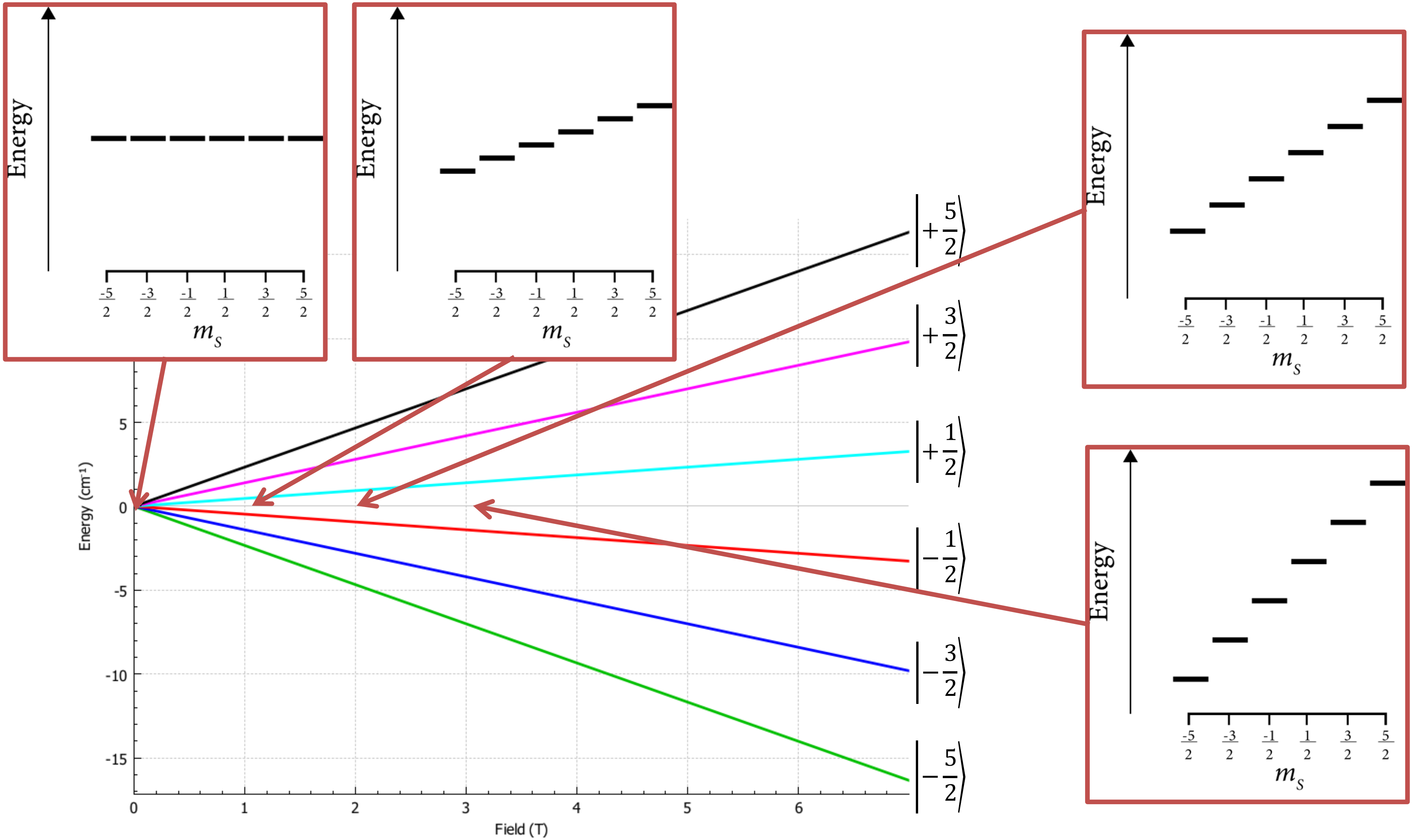
$\mu_B g m_S$

$g \approx 2$

$\mu_B \approx 0.467$ cm^{-1} T^{-1}

Zeeman effect

- Note how Zeeman diagram relates to the energy level diagram



Statistical mechanics

- How do we know which m_S state a given molecule is in?
- Boltzmann statistics tells us *probabilities* or *populations* in thermodynamic equilibrium
  - The partition function, *Z*:

$$Z = \sum_{i=1}^{dim} \exp\left[\frac{-E_i}{k_B T}\right]$$

  - The probability of a molecule being in state *i* or the fractional population of state *i* in the ensemble is:

$$p_i = \frac{1}{Z} \exp\left[\frac{-E_i}{k_B T}\right]$$

$$k_B \approx 0.695\ cm^{-1} K^{-1}$$

  - **ALWAYS set lowest energy as $E_i = 0$!**

Magnetisation (M)

- We measure the "magnetism" of a sample by its magnetisation:

$$M \propto -\frac{dE}{dB}$$

How magnetic field affects each state

Population of the state

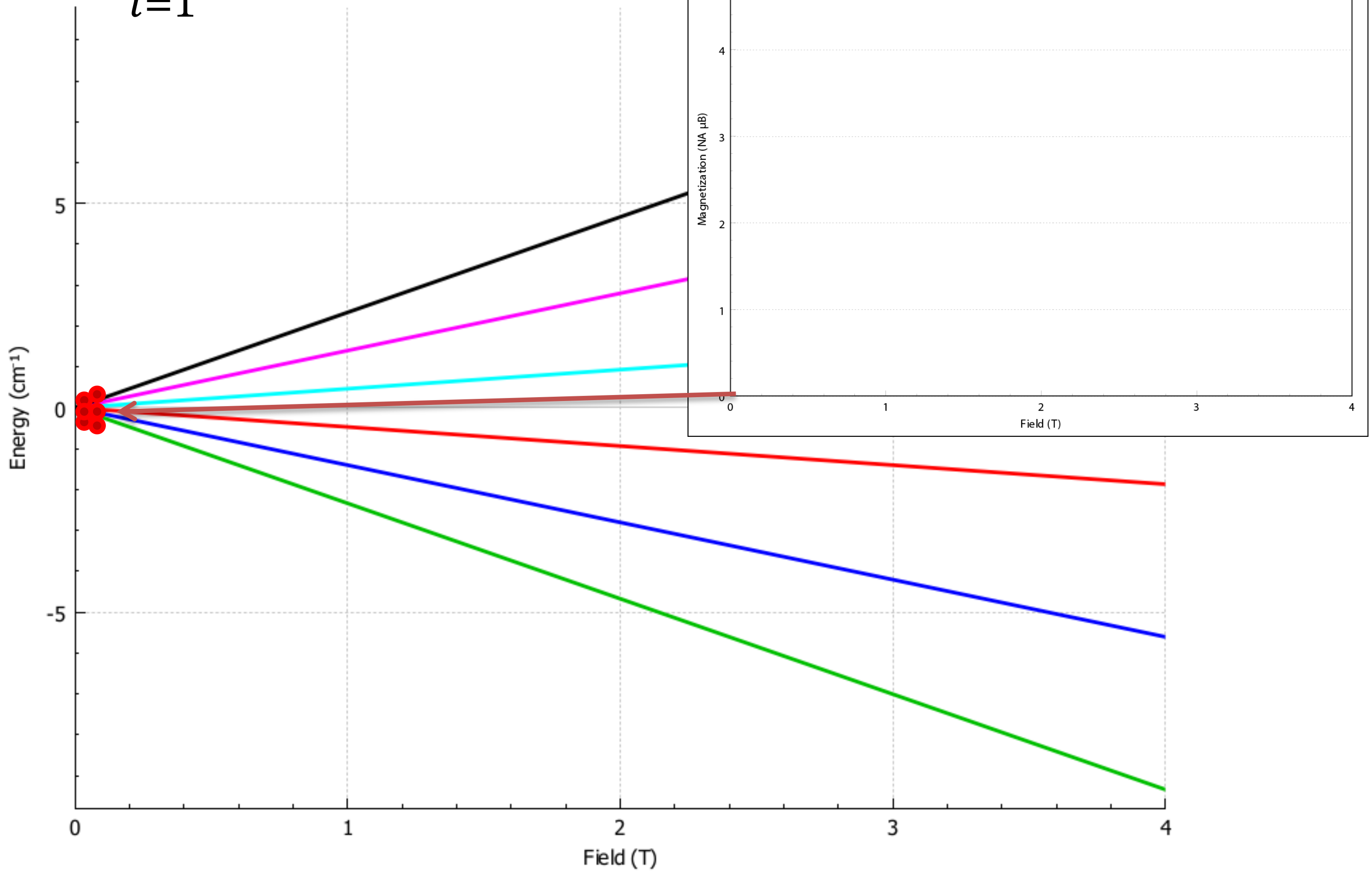
$$M = -\frac{1}{\mu_B}\sum_{i=1}^{dim}\left\{\frac{dE_i}{dB}\frac{1}{Z}\exp\left[\frac{-E_i}{k_B T}\right]\right\}$$

- Energy levels are functions of the magnetic field

- Units: $N_A \mu_B$

Magnetisation (M)

$$M = -\frac{1}{\mu_B}\sum_{i=1}^{dim}\left\{\frac{dE_i}{dB}\,\frac{1}{Z}\exp\left[\frac{-E_i}{k_BT}\right]\right\}$$



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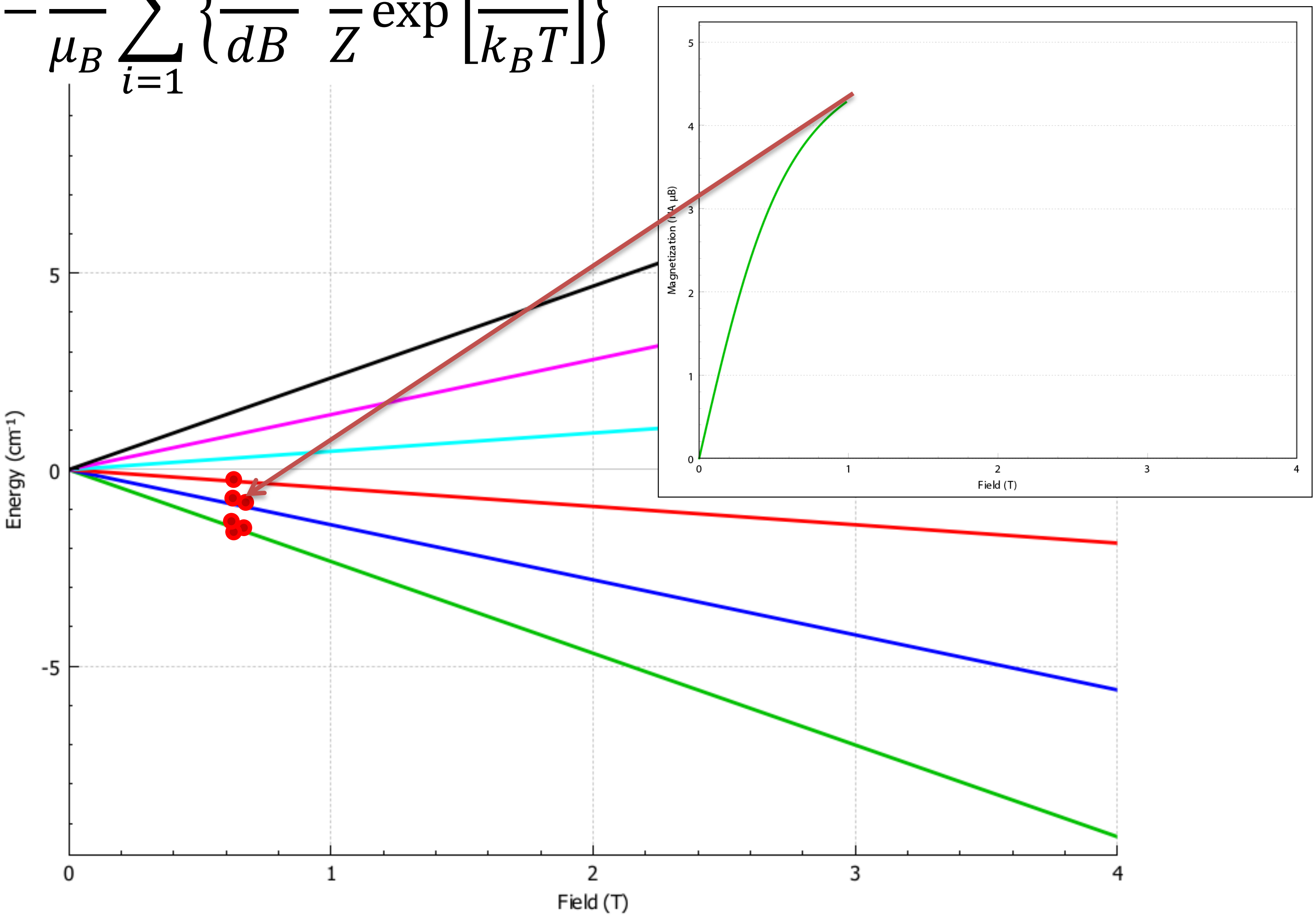

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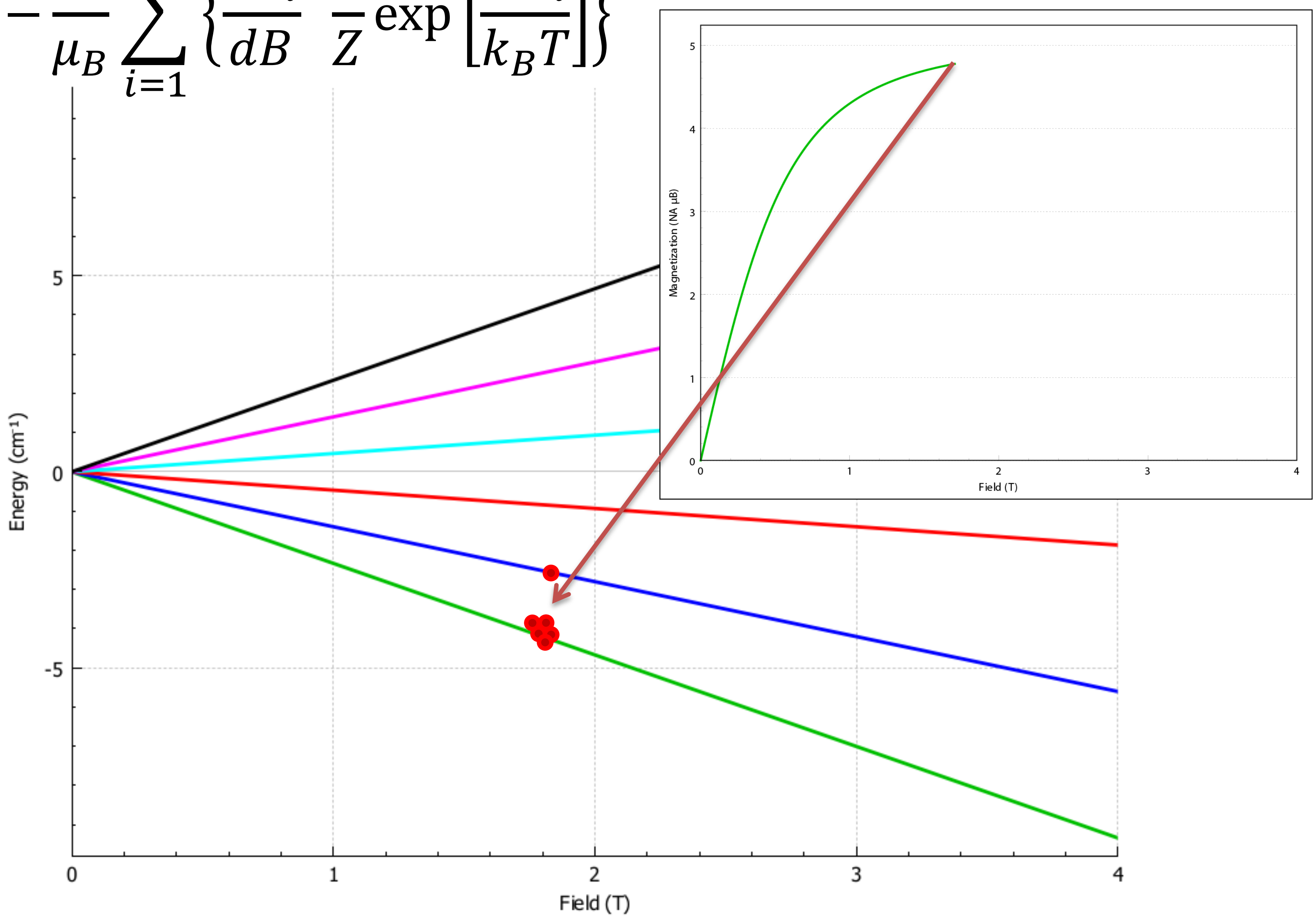

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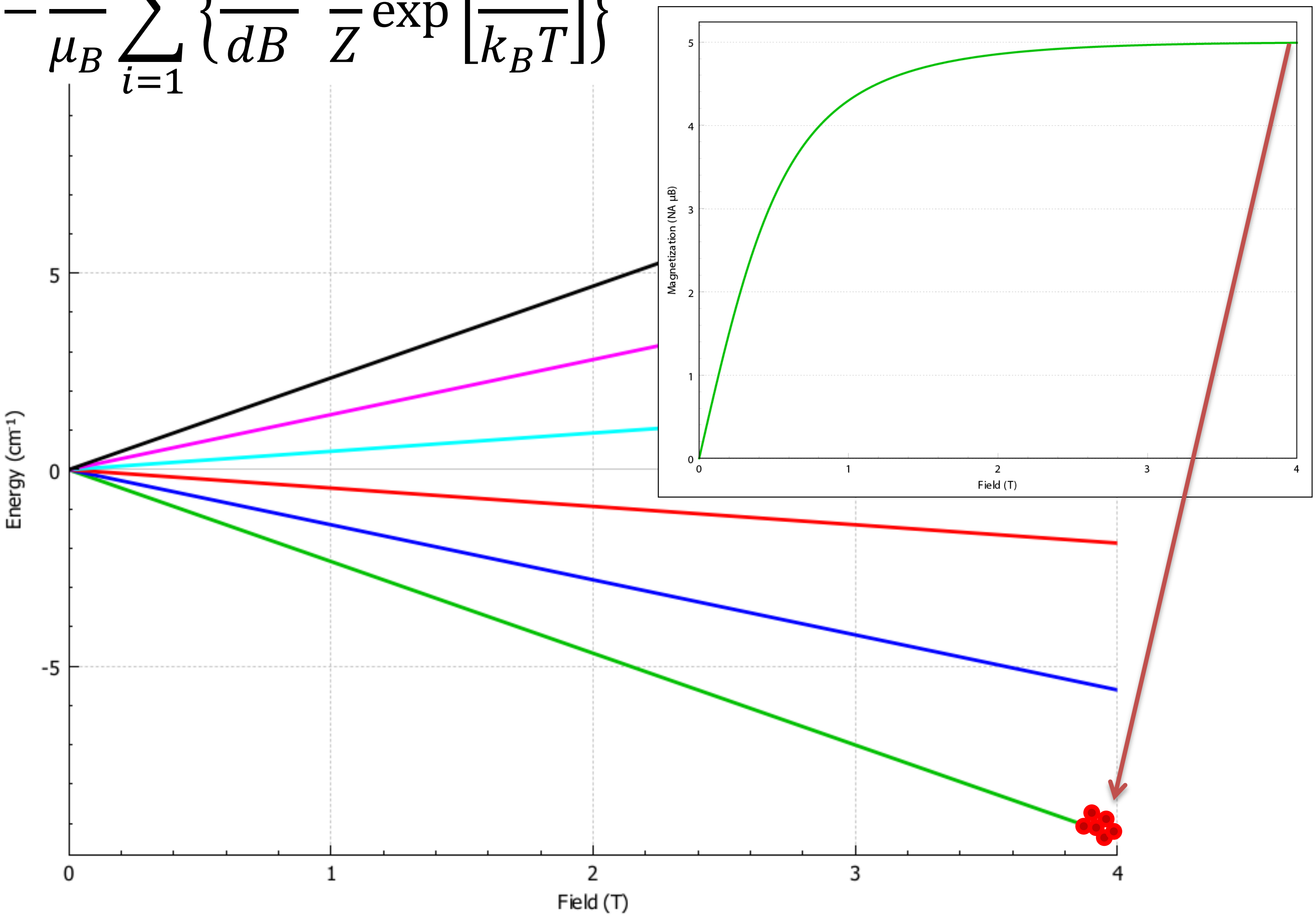

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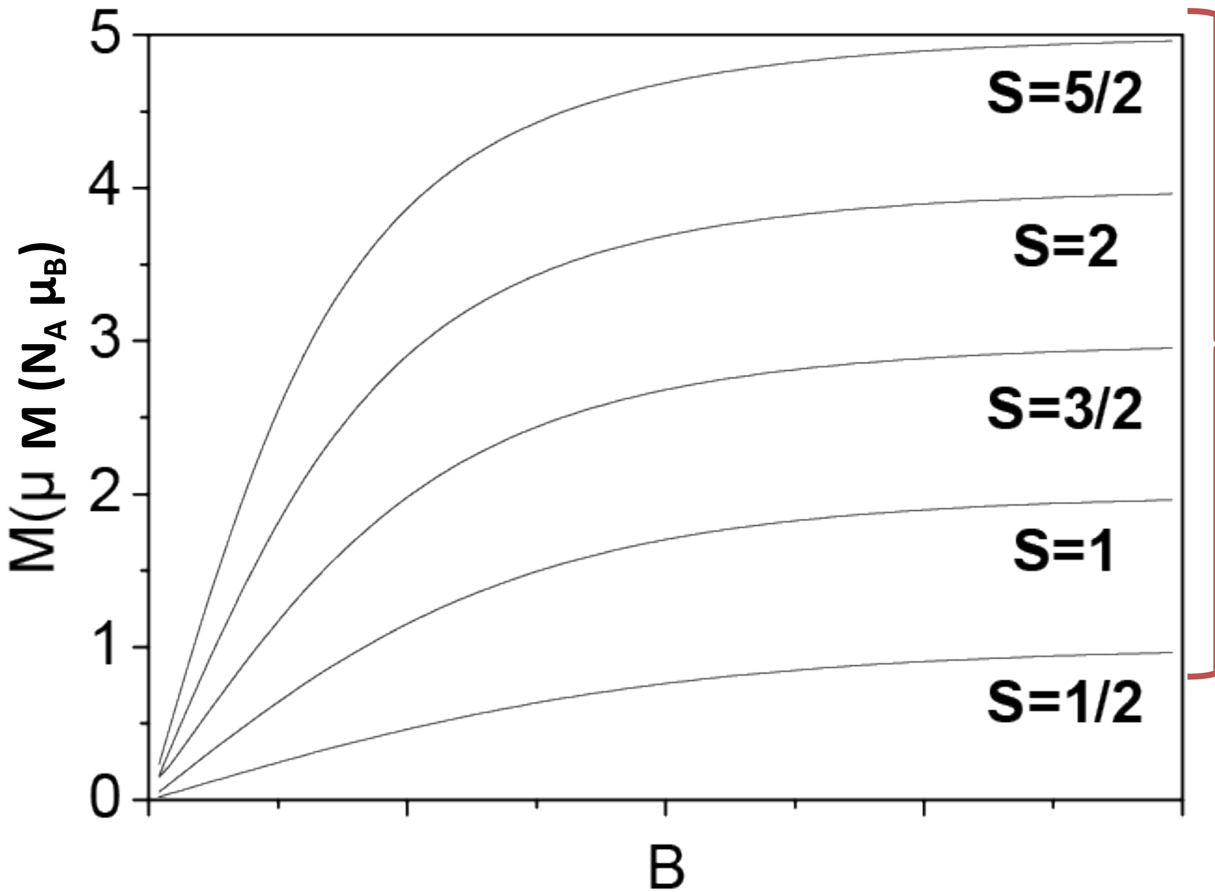


When all population in m_S = -S, magnetisation is *saturated*.

$M_{sat} \approx gS$ in μ_B units

Useful to determine S

Magnetic susceptibility (χ)

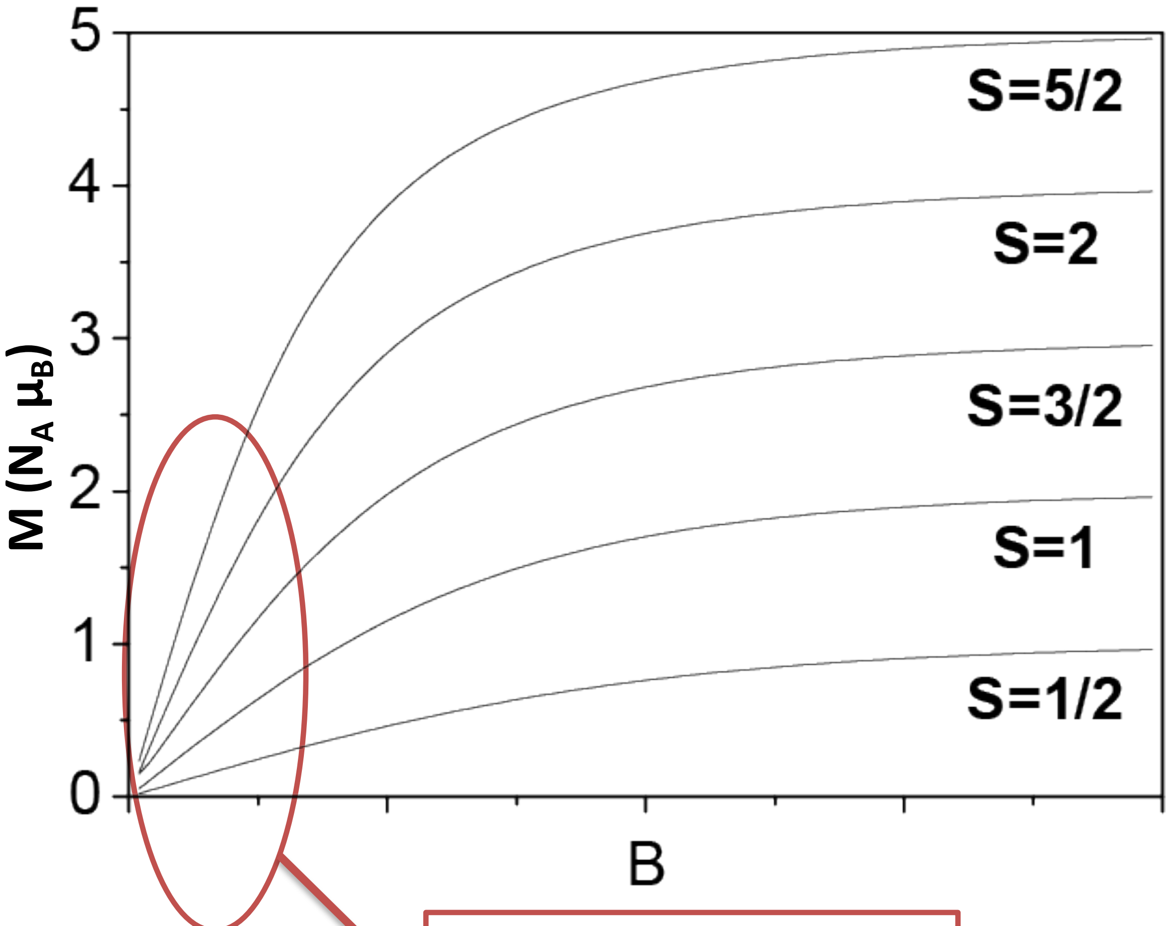
- Another useful quantity describes how easy it is to magnetise a sample:

$$\chi \propto \frac{dM}{dB}$$

$$\chi = \frac{N_A}{10k_BTZ^2}\left[Z\left(\sum_{i=1}^{dim}\left\{\left(\frac{dE_i}{dB}\right)^2 \exp\left[\frac{-E_i}{k_BT}\right]\right\} - k_BT\sum_{i=1}^{dim}\left\{\frac{d^2E_i}{dB^2}\exp\left[\frac{-E_i}{k_BT}\right]\right\}\right) - \left(\sum_{i=1}^{dim}\left\{\frac{dE_i}{dB}\exp\left[\frac{-E_i}{k_BT}\right]\right\}\right)^2\right]$$

- Units: $cm^3\ mol^{-1}$

Magnetic susceptibility (χ)



Linear at low field:
$\chi \approx 0.5585 \times M/B$

Magnetic susceptibility (χ)

- The empirical Curie law states:

$$\chi = \frac{C}{T}$$

- As the temperature drops, the sample becomes more susceptible to the magnetic field

- For perfect paramagnets:

$$C = \frac{{\mu_B}^2}{3k_B} N_A g^2 S(S+1) \approx \frac{g^2}{8} S(S+1)$$

Magnetic susceptibility (χ)

- Rearranging,

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

- Therefore if the Curie Law holds, χT vs. T should be constant

- As temperature is lowered we (usually) see deviations from Curie-like behaviour (this is where the fun happens)

Problem set:

- For $S = 1$ with $g = 2.1$:

1. What are the populations of the states at 0.1 T and 2 K?

2. What is the magnetisation at 0.1 T and 2 K?

3. What are the populations and magnetisation at zero field?

4. Using your answers from above, approximate the value of χT at 0.1 T and 2 K. Compare this to the value of the Curie constant.

Note: $\mu_B \approx 0.467$ cm^{-1} T^{-1} and $k_B \approx 0.695\ cm^{-1}K^{-1}$