PHI:
Theory and application

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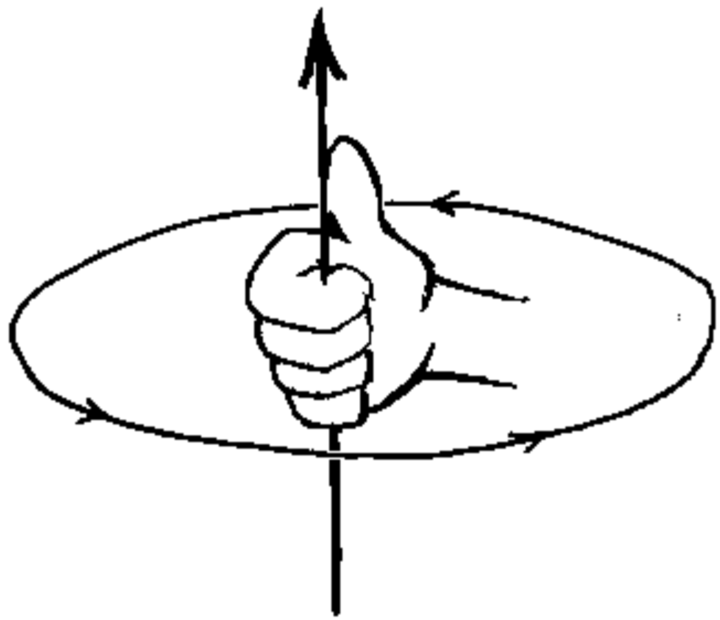
Electrons

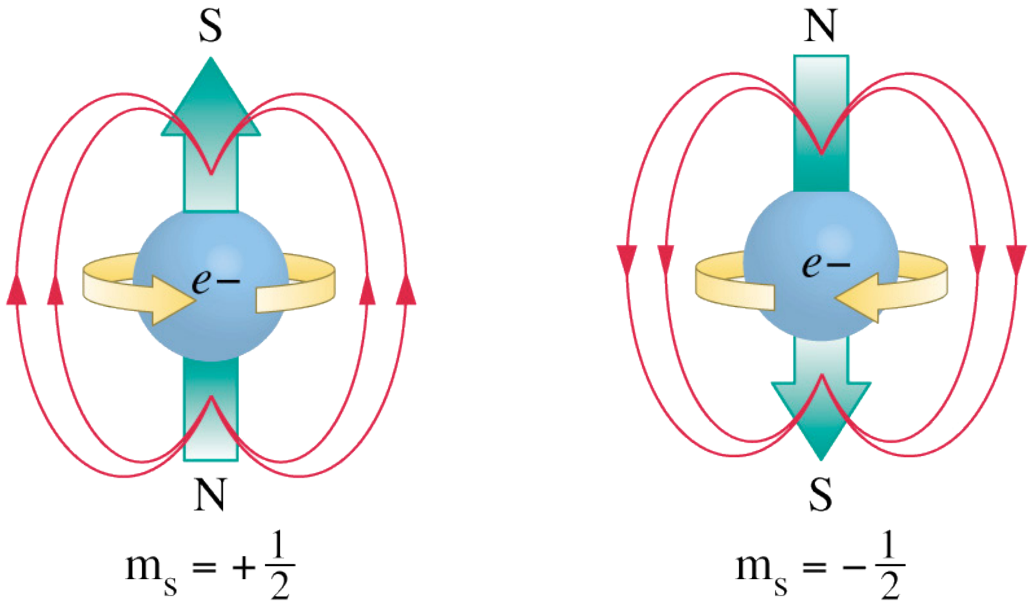
- Movement of electrons (current) generates a magnetic field (orbital magnetic moment)



- Orbital moment is inherently physical – occurs due to physical motion

Electrons

- Intrinsic ‘spin’ of the electron creates a magnetic moment (spin magnetic moment)



Note: the depiction of electrons spinning on their axes is just a pictorial representation, as electrons do not have physical dimensions!

- Spin moment is non-physical – the spin degree of freedom exists in an isolated space

Electrons

Wavefunctions and Hamiltonians

- The Wavefunction encodes all information about the system
- Determines behaviour in future
- Probabilistic interpretation

$$\hat{H}\Psi = E\Psi$$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\Psi = E\,\Psi$$

Wavefunctions and Hamiltonians

- *Ab-initio* approaches consider the entire picture of all electrons within a molecular orbital basis
- The full Hamiltonian contains all the interactions of the system (within some approximations and simplifications)

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\Psi = E\,\Psi$$

Wavefunctions and Hamiltonians

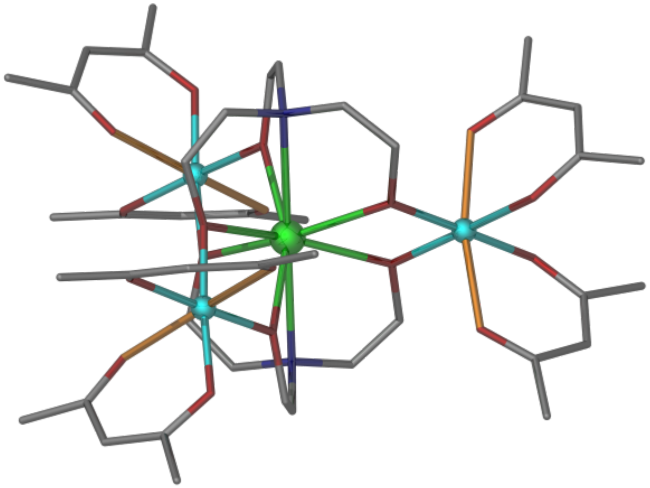
Spin Hamiltonians

» The Spin Hamiltonian approach approximates the complete Hamiltonian with an effective Hamiltonian

» We limit our description of the system (molecule) to only the paramagnetic ion(s)

» Simplifies the analysis

» Inherently phenomenological (meaning parameters must be determined from experiment and not known *ab-initio*)



3 x S_{Mn}, 1 x S_{Gd}

Spin Hamiltonians

Free Atoms (Ions)

» We consider only a subspace of the total wavefunction, based on the single configuration approximation

$$3d^2 \in \{3d^2, 3d^1 4s^1, etc.\}$$

» Furthermore, within the single configuration approximation, we consider only the total spin and orbital terms (Russell-Saunders or LS coupling)

$$S = \sum_i s_i \, , L = \sum_i l_i \longrightarrow {}^{2S+1}L_J$$

Free Atoms (Ions)

- These terms are separated in energy by the electron-electron repulsion (Coulomb term)

- The terms only specify the angular components of the wavefunction

- Integrals over the radial components are absorbed into the Spin Hamiltonian parameters

Free Atoms (Ions)

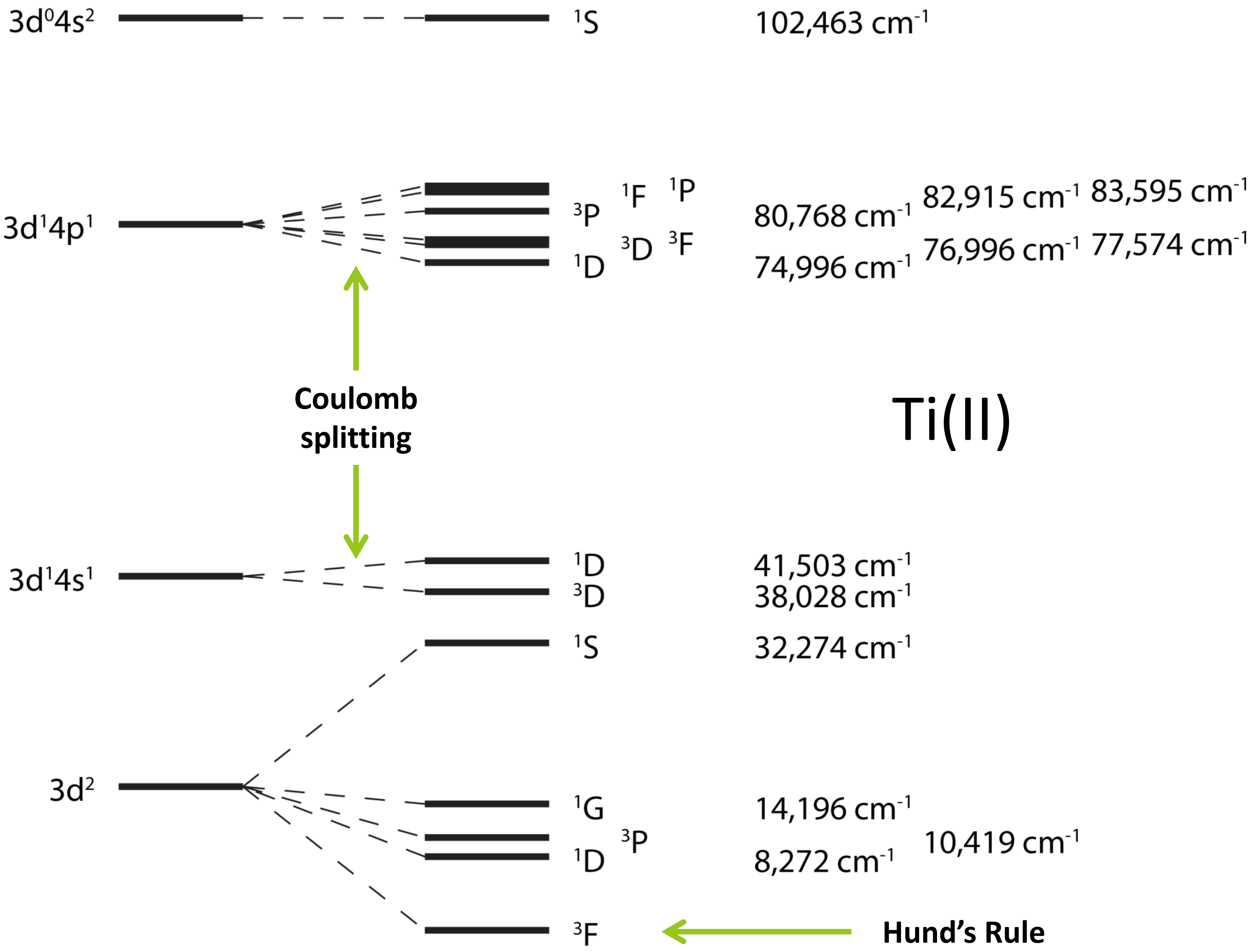
» In this case, we only consider the ground term

» Why? Magnetic measurements are thermodynamic quantities, accessible energies are set by the temperature

» Properties determined by low-energy structure

» Different when considering spectroscopic properties

Free Atoms (Ions)



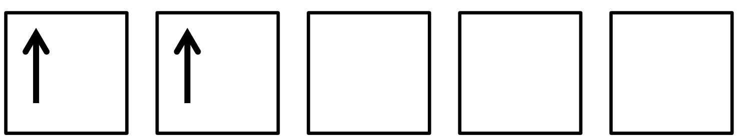
3d0 4s2
1S
102,463 cm-1
3d1 4p1
3P
1F
1P
3D
3F
1D
80,768 cm-1
82,915 cm-1
83,595 cm-1
74,996 cm-1
76,996 cm-1
77,574 cm-1
Coulomb splitting
Ti(II)
3d1 4s1
1D
3D
41,503 cm-1
38,028 cm-1
1S
32,274 cm-1
3d2
1G
14,196 cm-1
3P
10,419 cm-1
1D
8,272 cm-1
3F
Hund's Rule

» How do we determine the ground term?

» Take the configuration $3d^2$

» Place electrons in orbitals following the Pauli exclusion principle (no electrons with same set of quantum numbers) and Hund’s Rules (largest S and L)

$$l = \;2 \quad 1 \quad 0 \quad -1 \quad -2$$



$$^3F$$

Free Atoms (Ions)

- We have two magnetic moments – spin and orbital and we know that magnetic moments affect each other…
- We get spin-orbit coupling, which is actually a relativistic effect
- Couples spin and orbital momentum of single electrons

$$\hat{H}_{SO} = \sum_i \zeta l_i \cdot s_i \approx \lambda L \cdot S$$

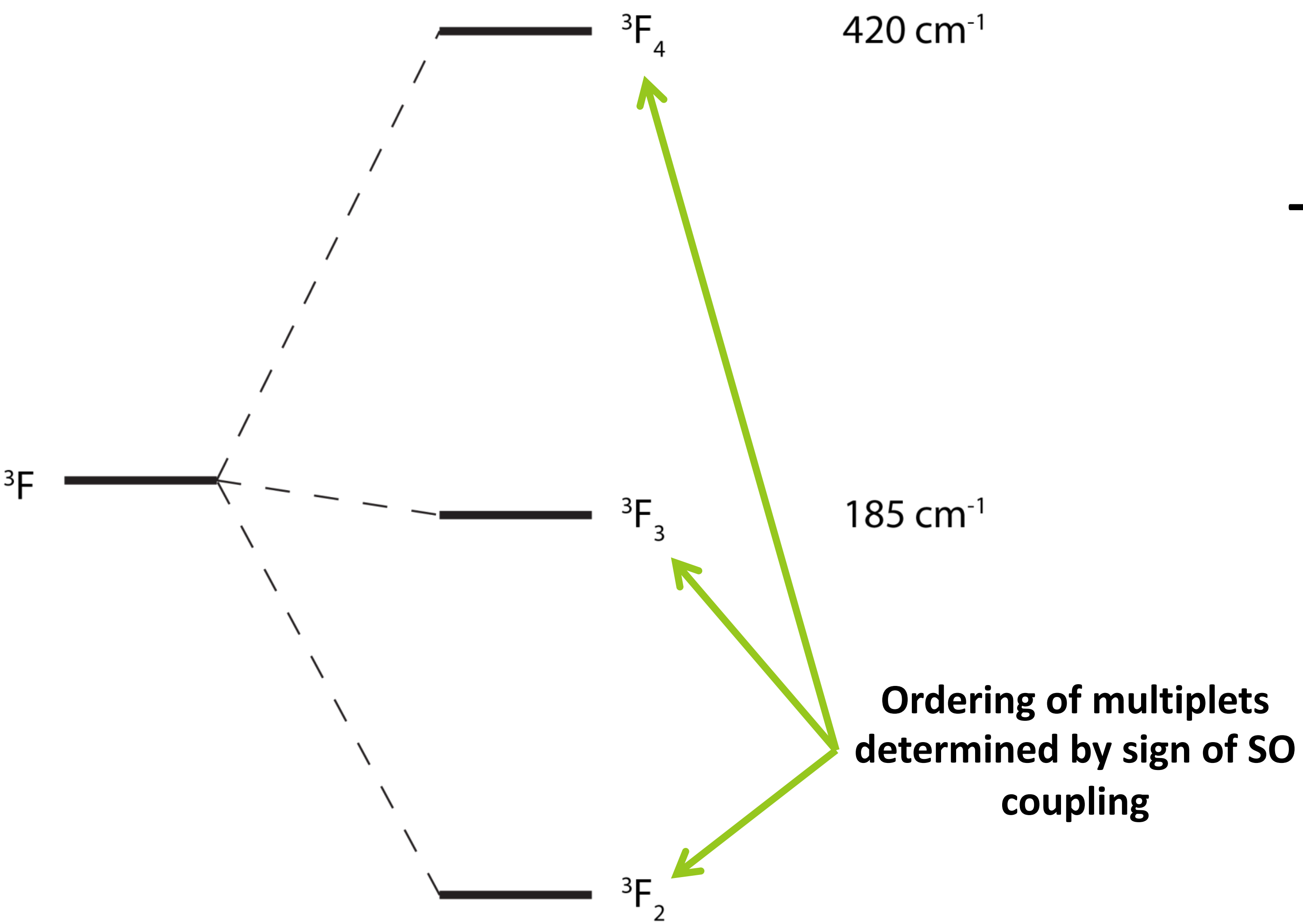
- Becomes more important with heavier elements
- Often treated as a perturbation to terms

Free Atoms (Ions)

$$^3F, S = 1, L = 3$$

$$J = |L - S|, |L - S| + 1, \ldots, L + S - 1, L + S$$

$$J = 2, 3, 4$$



Ti(II)

» $\lambda > 0$ for a less than half filled shell

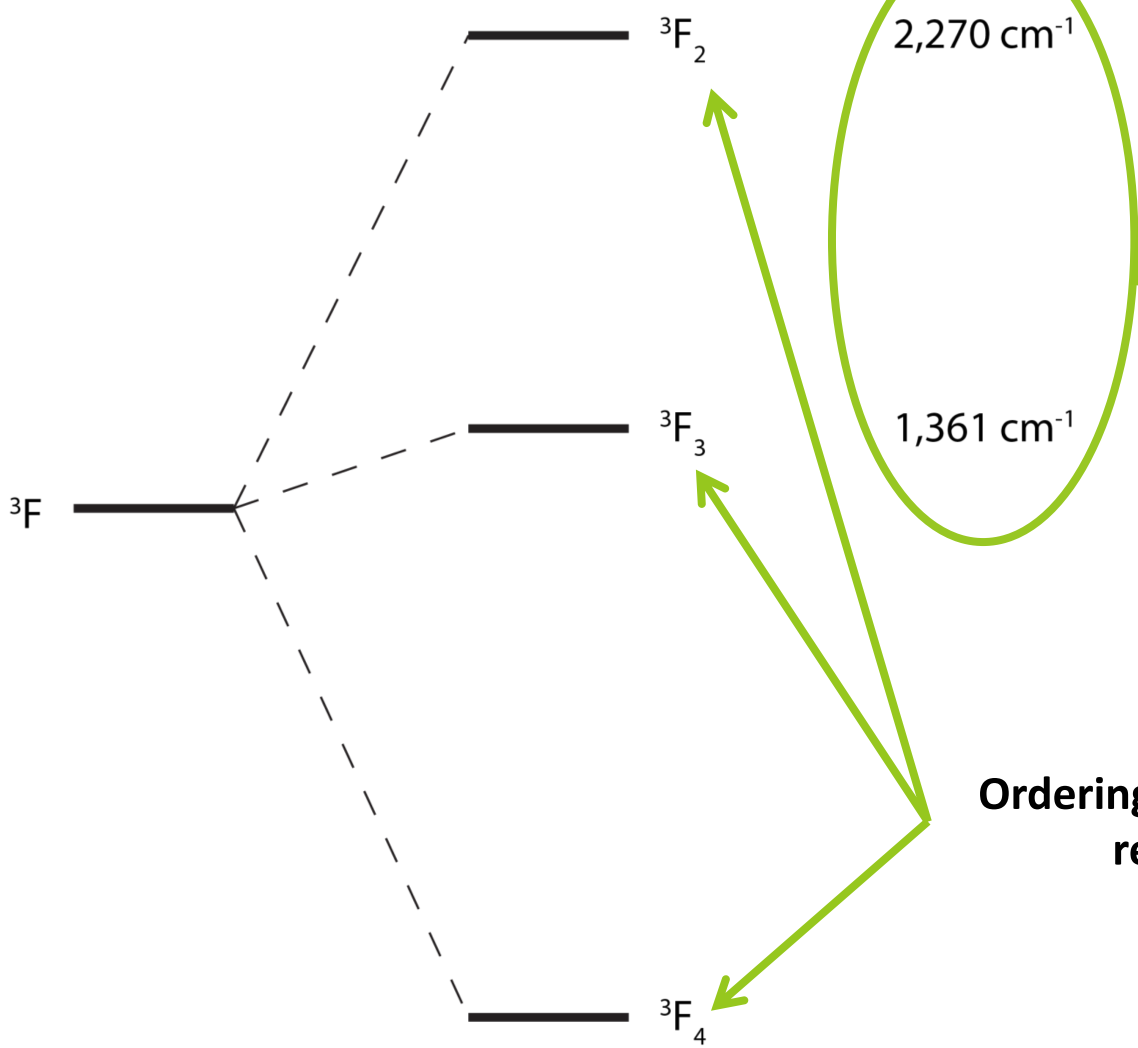
» $\lambda < 0$ for a more than half filled shell

» Therefore, the maximum *J* is the ground state for ions with a more than half filled shell

Free Atoms (Ions)

SO splitting larger due to higher mass

$$\lambda_{Ti(II)} \approx 155\ cm^{-1}, \lambda_{Ni(II)} \approx -315\ cm^{-1}$$



Ni(II)

d^8 configuration, analogous to d^2

Ordering of multiplets reversed

Crystal Fields

» The effect of ligands due to bonding and electrostatic interactions cannot be ignored

» Strikingly different effects for metals in different blocks

» Ligands strongly interact with 3d orbitals

$$\hat{H}_{EE} \sim \hat{H}_{CF} > \hat{H}_{SO}$$

» Ligands only weakly influence 4f orbitals

$$\hat{H}_{EE} > \hat{H}_{SO} > \hat{H}_{CF}$$

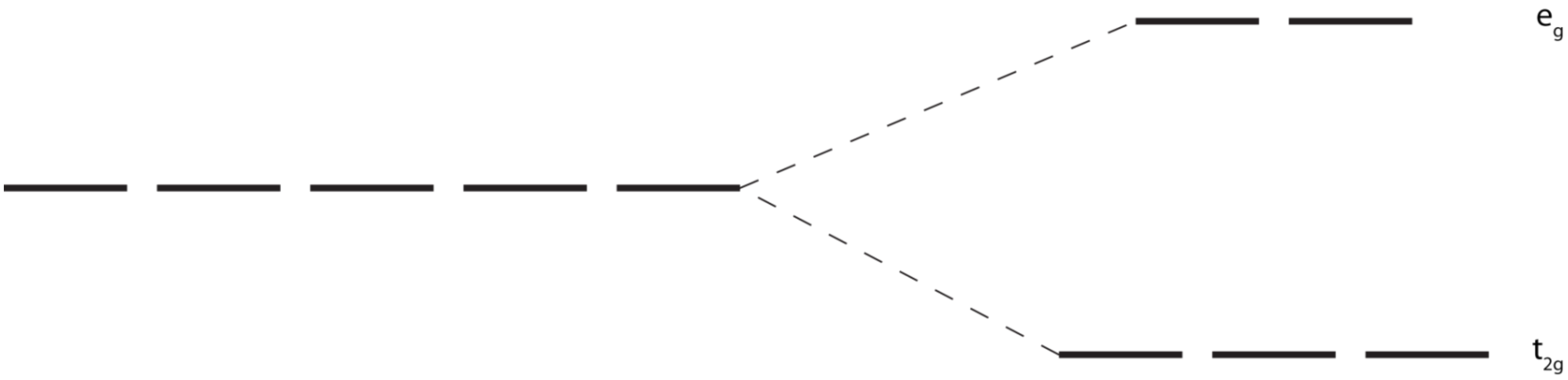
» Intermediate behaviour for 4d, 5d and 5f

$$\hat{H}_{EE} \sim \hat{H}_{SO} \sim \hat{H}_{CF}$$

Crystal Fields

3d Crystal Fields

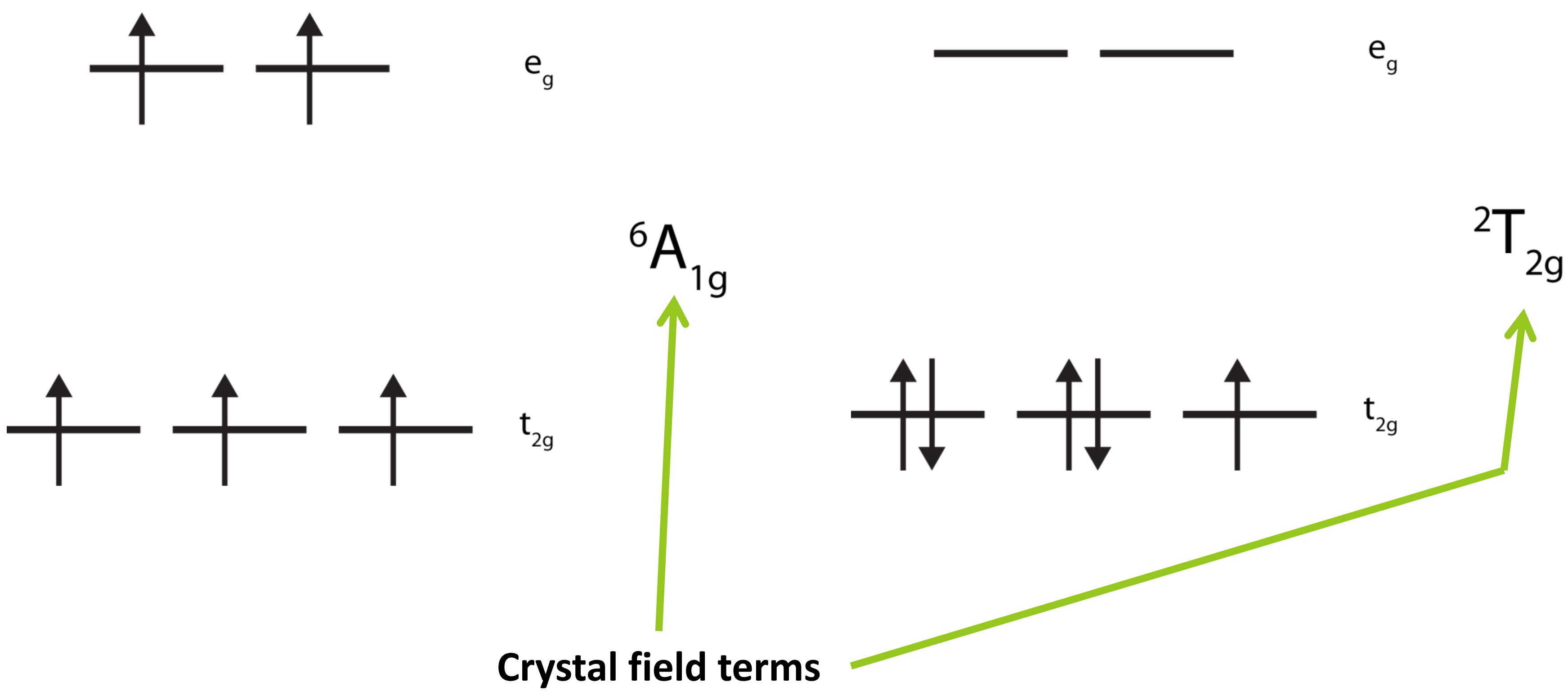
- Octahedral coordination, O_h symmetry



- Depending on strength of splitting, this can redefine orbital population and therefore changes the terms
- Splitting depends on symmetry
- Distortions can be perturbations
- For 3d ions in complexes, we must therefore consider:
  - the coordination geometry
  - if the ion is ‘high-spin’ or ‘low-spin’

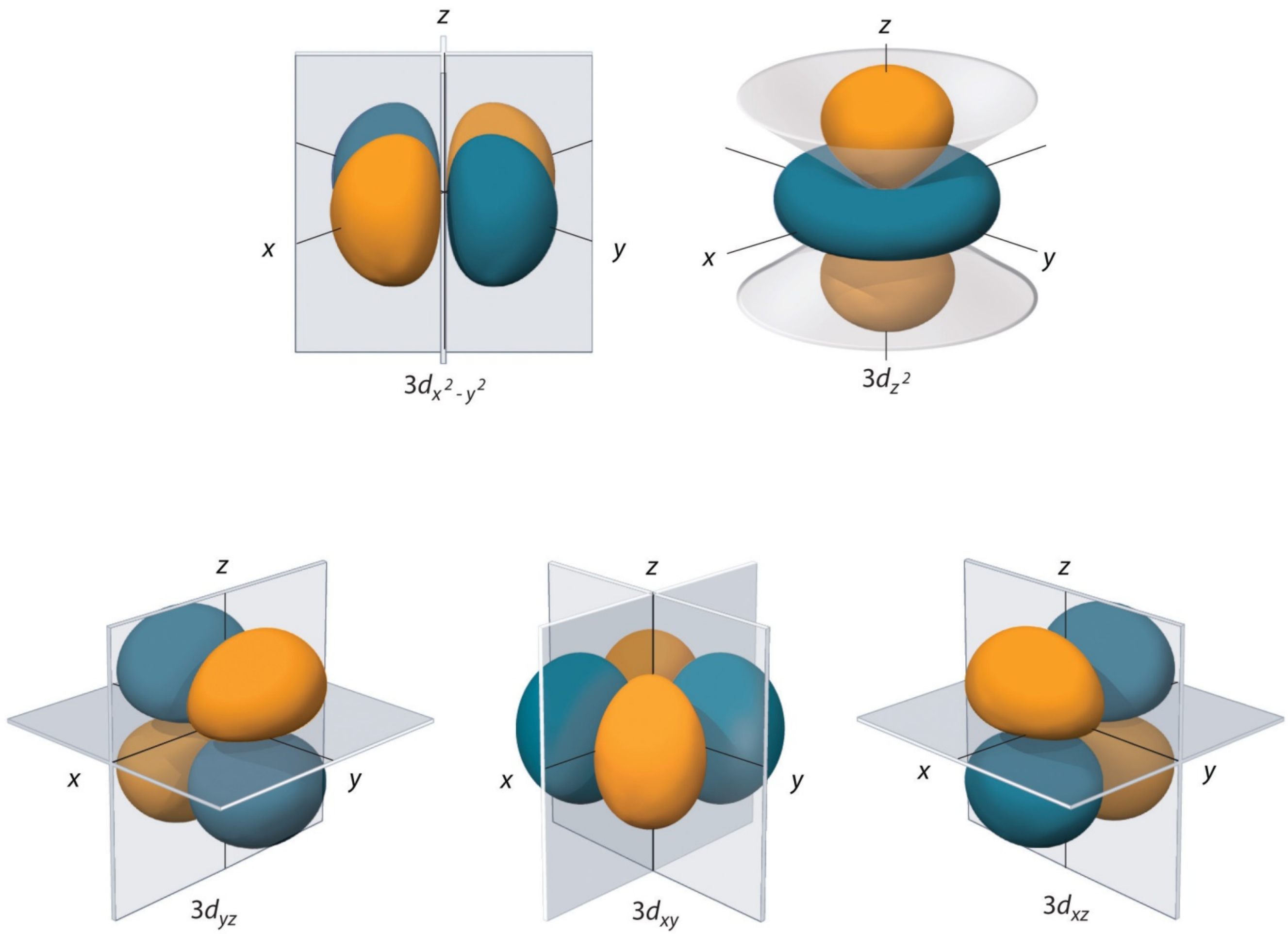
3d Crystal Fields

» For Fe(III) in an octahedral environment, there are two options:



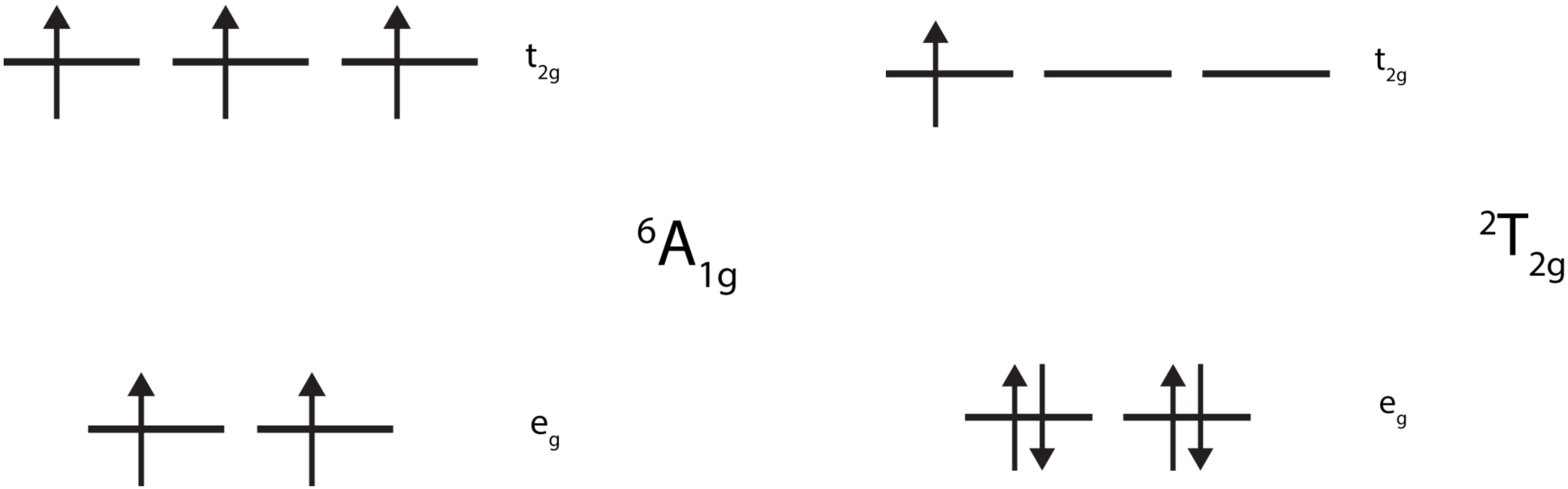
3d Crystal Fields

» Think about the t_{2g} orbitals:



3d Crystal Fields

» What about for tetrahedral Fe(III)?:



3d Crystal Fields

» So for cubic Fe(III):

» $^6A_{1g}$ term: $S = {}^5/_2$, $L = 0$

» $^2T_{2g}$ term: $S = {}^1/_2$, $L = ?$

» Cubic triplet terms have first order orbital angular momentum, but do not easily correspond to free-ion terms…

T, P Equivalence

» The matrix elements of orbital angular momentum are the same for cubic triplet terms and P terms

» So we can treat triplet terms as L = 1

» However, there is a catch: T ≠ P, therefore we need a constant of proportionality, *A*

» For T_2 terms $A = -1$

» For T_1 terms $A = -^3/_2$

T, P Equivalence

T, P Equivalence

- Strong crystal field interaction means substantial orbital mixing
- Low symmetry distortions also affect orbitals

- While spins are not affected (unless d electrons form bonds), the effective orbital moment is reduced

- This is known as orbital reduction, k
- $0 \leq k \leq 1$ and is lower for stronger covalency
- Typically, $0.70 \leq k \leq 0.95$
- Together with the T, P constant, $\sigma = kA$
- Often regarded as a ‘fudge factor’, but can sometimes contain very important science

4f Crystal Fields

4f Crystal Fields

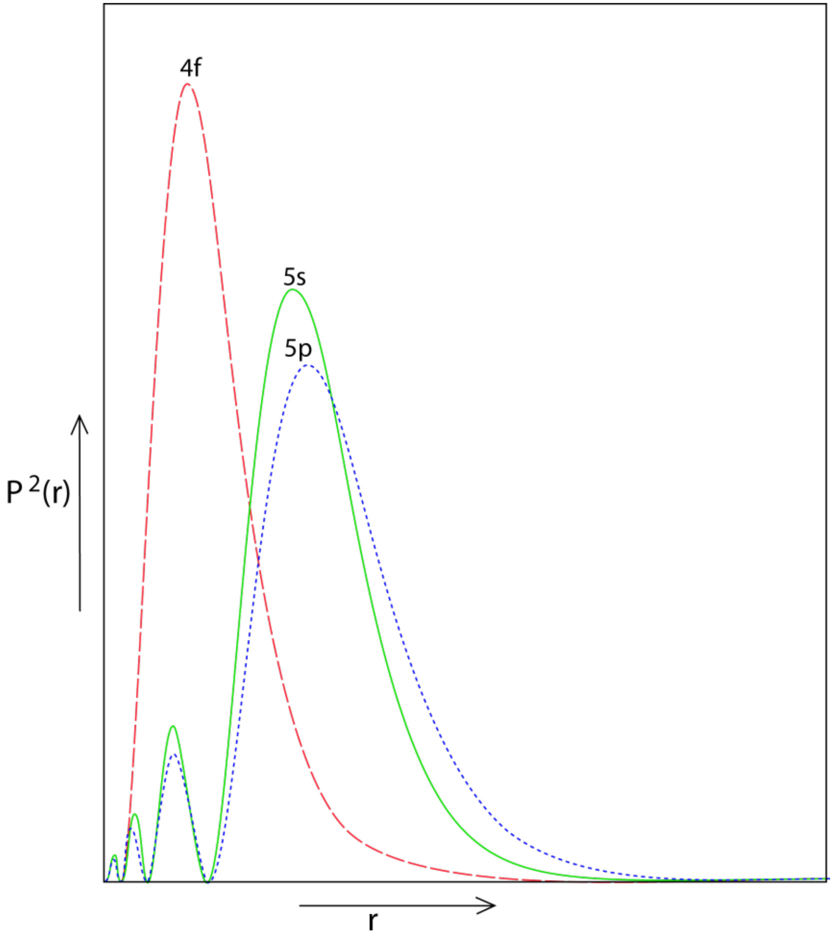
» The 4f orbitals are well shielded by the full 5s and 5p orbitals

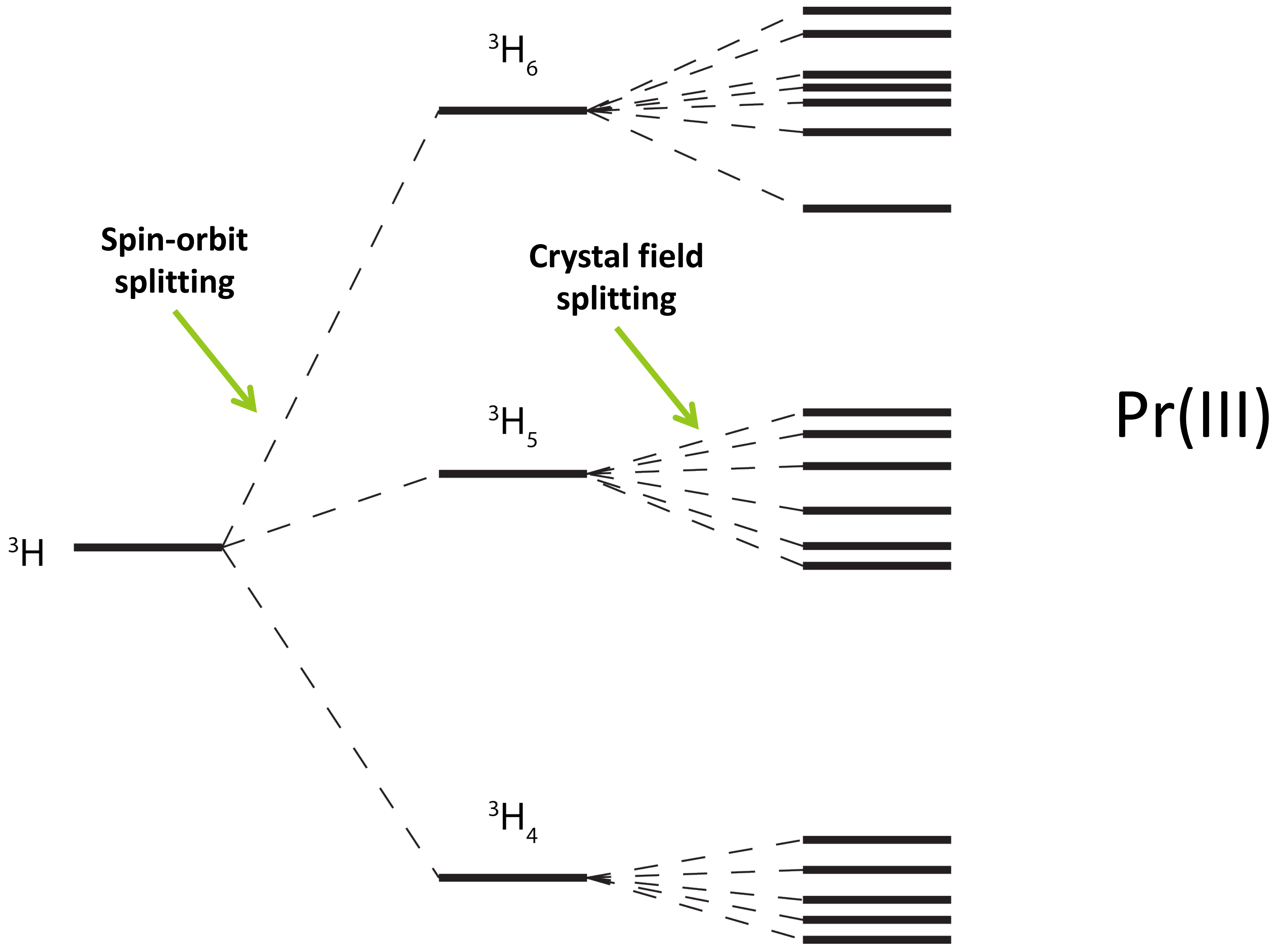
» Therefore, 4f orbitals are not really effected

» Spin-orbit multiplets are split

» Spin-orbit ≈ 2 – 6 kcm^{-1}

» Crystal field ≈ < 1 kcm^{-1}





^3H
Spin-orbit splitting
$^3H_6$
$^3H_5$
$^3H_4$
Crystal field splitting
Pr(III)

Exchange

Exchange

- Magnetic interactions between paramagnetic ions can be due to a number of physical phenomena:

- Direct exchange (overlap of magnetic orbitals)
- Super exchange (interaction through diamagnetic bridge)
- Dipolar interactions (through space)

- Orbital moment interactions are very complex and will not be covered

- These interactions lead to isotropic, anisotropic and anti-symmetric components
- Almost impossible to completely unravel without a combined magnetic and detailed spectroscopic analysis

- We will focus on isotropic interactions only

Exchange

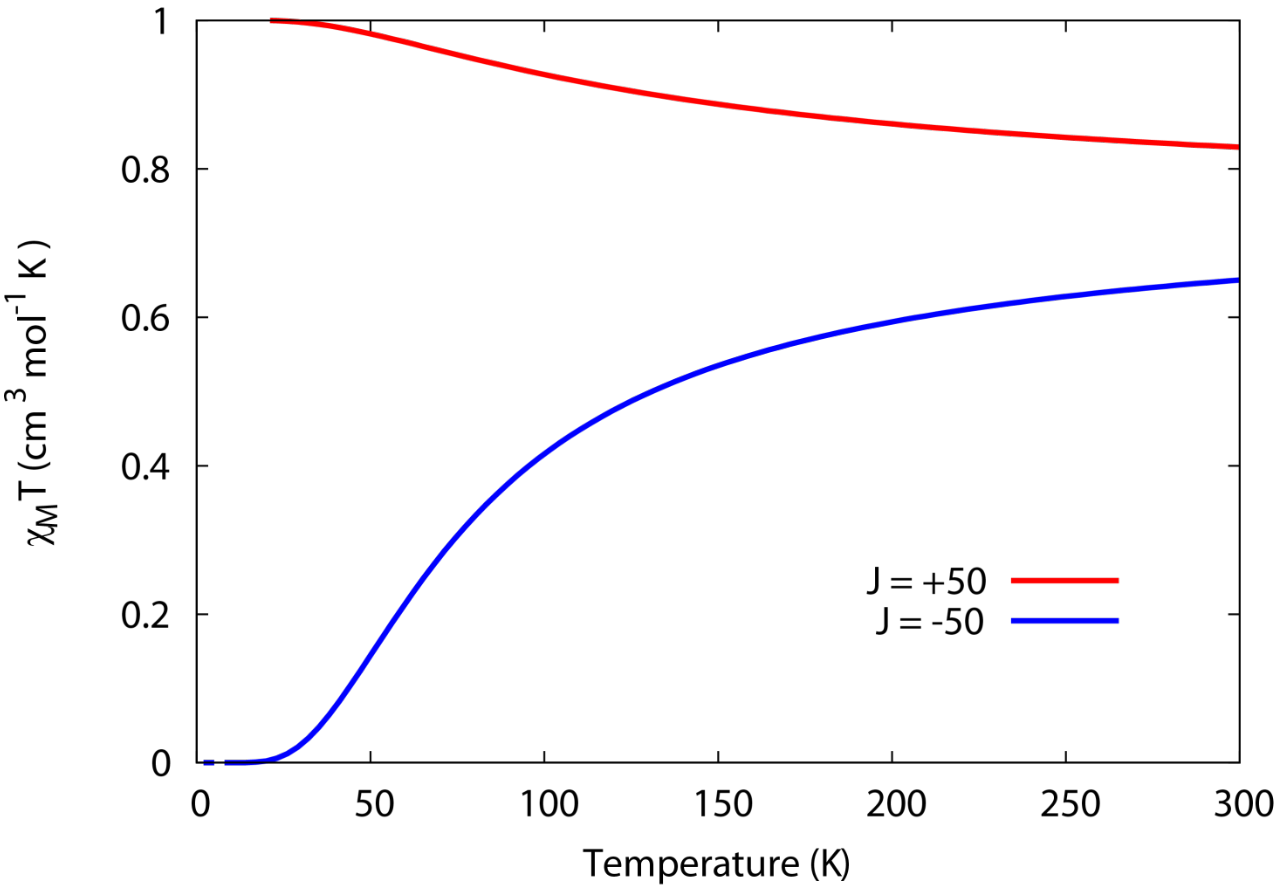
» Isotropic interaction between two spins is simple:
» Spins are parallel (ferromagnetic)
» Spins are anti-parallel (anti-ferromagnetic)

» Both states exist, just one is more energetically stable than the other
» The magnitude of the exchange interaction sets the gap between these two possibilities

» Only care about the relative energies, hence we do not need to know the (real) absolute energies!
» This is why we can essentially ignore the rest of the molecule!

Exchange

» Easy to see the effect on the system:



Exchange

» Interaction between multiple spins becomes complicated (hence PHI!)

» Many possible configurations of individual spins

» Frustration, degeneracy, etc.

» Leads to total spin of cluster

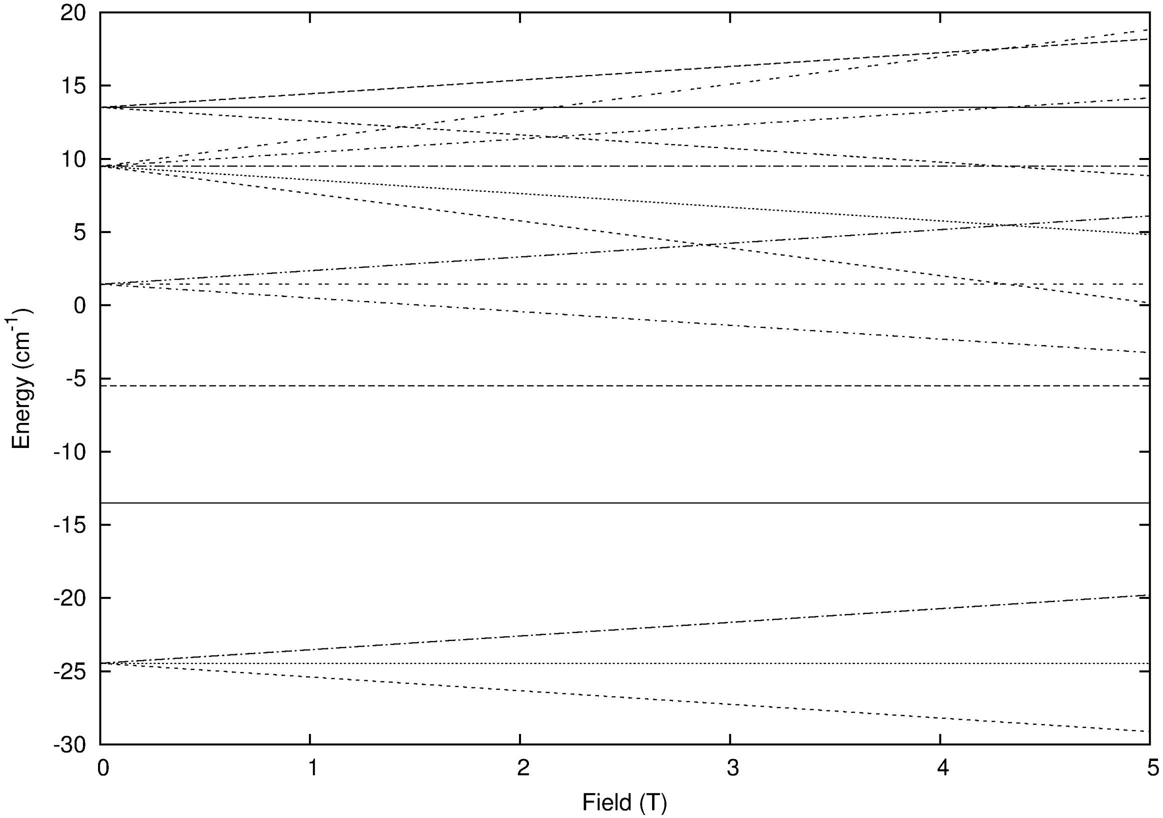
» Exchange for 3d ions from 1 – 100’s cm^{-1}

» Exchange for 4f ions from < 2 cm^{-1} (usually)

Exchange

Zeeman Effect

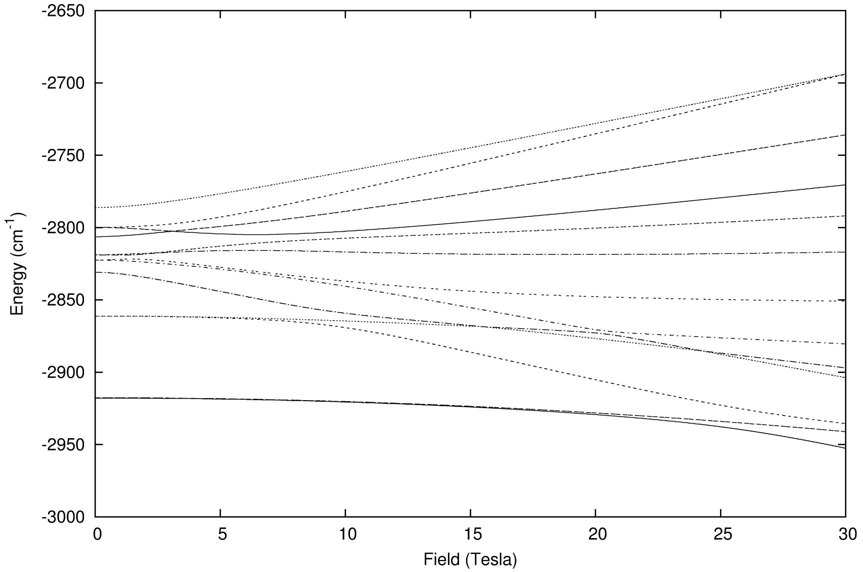
- A magnetic field will cause magnetic moments to align
- In other words, moments anti-parallel to the magnetic field are in a higher energy state than those parallel to the field



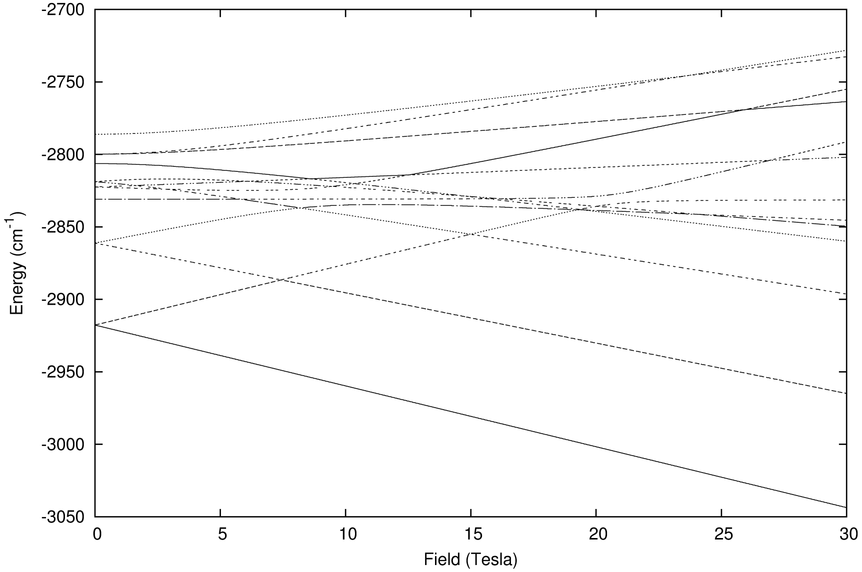
- This effect gives rise to all magnetic observables, makes NMR, MRI, EPR, etc. possible

Zeeman Effect

- Only a linear effect when the magnetic field is small compared to the interactions within the system
- Can be anisotropic and non-linear in low field as well!



$TbCl_3$ x-direction



$TbCl_3$ z-direction

Zeeman Effect

The Spin Hamiltonian

…but first some terminology

Terminology

- Operator
  - Mathematical function which changes an object
- Eigenvector (Eigenfunction)
  - A combination of basis states
- Eigenvalue
  - The energy corresponding to an eigenvector
- Wavefunction
  - Collection of eigenvectors of the Hamiltonian
- Basis
  - Complete set of possible states
- Ket
  - A vector (usually a unit vector of one of the basis states)

…and some notation

- A
  - Scalar
- $\hat{A}$
  - Operator
- $\vec{\hat{A}} = (\hat{A}_x, \hat{A}_y, \hat{A}_z)$
  - Vector operator
- $\hat{A}_\alpha$
  - Component of vector operator
- $\bar{\bar{A}}$
  - Matrix

Notation

The Spin Hamiltonian

$$\hat{H}\overrightarrow{\Psi} = E\overrightarrow{\Psi}$$

$$\hat{H} = \hat{H}_{SO} + \hat{H}_{EX} + \hat{H}_{ZEE} + \hat{H}_{CF}$$

Spin-orbit coupling

Exchange

Zeeman effect

Crystal Field

The Spin Hamiltonian

$$\hat{H}_{SO} = \sum_{i=1}^{N} \sum_{j=1}^{2S_i} \lambda_{j_i} \left(\sigma_i \vec{\hat{L}}_i \cdot \vec{\hat{S}}_i \right)^{j}$$

Sum over all ions

Higher orders required for heavy metals

Orbital reduction

Operators

Spin-orbit coupling parameters

The Spin Hamiltonian

$$\hat{H}_{EX} = -2 \sum_{i<j}^{i,j \in N} \vec{\hat{S}}_i \cdot \overline{\overline{J_{ij}}} \cdot \vec{\hat{S}}_j$$

Count pairs only once

Sum over all ions

Exchange parameters

Operators

$$\hat{H}_{EX} = \hat{H}_{(an)iso} + \hat{H}_{anti}$$

The Spin Hamiltonian

$$\hat{H}_{iso} = -2 \sum_{i<j}^{i,j\in N} J_{ij} \vec{\hat{S}}_i \cdot \vec{\hat{S}}_j$$

Count pairs only once

Sum over all ions

Exchange parameters

Operators

The Spin Hamiltonian

$$\hat{H}_{ZEE} = \mu_B \sum_{i=1}^{N} \left(\sigma_i \bar{\hat{L}}_i \cdot I + \bar{\hat{S}}_i \cdot g_i \right) \cdot \vec{B}$$

Sum over all ions

Orbital reduction

Operators

***g*-tensor**

Magnetic field

The Spin Hamiltonian

$$\hat{H}_{CF} = \sum_{i=1}^{N} \sum_{k=2,4,6} \sum_{q=-k}^{k} B_{k\,i}^{q}\, \theta_k\, \hat{O}_{k\,i}^{q}$$

Sum over all ions

Components of the crystal field as limited by symmetry, parity and the single configuration approximation

Crystal field parameters

Operator equivalent factors

Operators (containing orbital reduction parameter)

The Spin Hamiltonian

» The Crystal Field Hamiltonian is very closely related to the common Zero Field Splitting Hamiltonian of EPR

$$\vec{\hat{S}} \cdot \overline{\overline{D}} \cdot \vec{\hat{S}} = D\left(\hat{S}_z^2 - \frac{1}{3}S(S+1)\right) + \mathrm{E}\left(\hat{S}_+^2 + \hat{S}_-^2\right)$$

$$\hat{O}_2^0 = 3\hat{S}_z^2 - S(S+1)$$

$$\hat{O}_2^2 = \hat{S}_+^2 + \hat{S}_-^2$$

» Therefore,

$$B_2^0\theta_2 = \frac{D}{3}$$

$$B_2^2\theta_2 = E$$

The Spin Hamiltonian

- However, it is important to note that spin magnetic moments are not directly perturbed by the environment!

- Remember, spins don’t exist in ‘real space’ and so the ZFS of a spin ground state is due to the fact that it isn’t completely a ‘spin only’ state!
- Mixing with excited states that have orbital components (and therefore CF interactions) is the origin of the ZFS

- It is just convenient to parameterize it in the same way as the CF

The Wavefunction

» How to solve the equation? How do we find Ψ?

$$\widehat{H}\overrightarrow{\Psi} = E\overrightarrow{\Psi}$$

» We know the term(s), therefore we know the spin and orbital components

$$m_L = -L, -L+1, \ldots, L-1, L$$
$$m_S = -S, -S+1, \ldots, S-1, S$$

» We construct a space with all the possible combinations (Hilbert Space)

The Wavefunction

- ${}^3F$ term of Ti(II): $S = 1$, $L = 3$
- Therefore, $m_S = -1, 0, 1$

  and $m_L = -3, -2, -1, 0, 1, 2, 3$

- The total number of combinations is 3 x 7 = 21
- In general, the dimension of the Hilbert space is

$$dim = \prod_{i}^{N} (2S_i + 1)(2L_i + 1)$$

$$= (2S_1 + 1)(2L_1 + 1)(2S_2 + 1)(2L_2 + 1) \ldots$$

- Each of these different combinations is orthogonal – that is, all elements of the set are unique

The Wavefunction

» This defines what is called a 'basis'

» The 'basis states' are the different combinations of m_L and m_S

» They are often written in bra-ket notation

$$|m_L, m_S\rangle \equiv |\omega, L, S, m_L, m_S\rangle$$

» where ω denotes any other quantum numbers to identify the state uniquely

» So for our example,

$$|m_L, m_S\rangle \equiv |3d^2, 3,1, m_L, m_S\rangle$$

The Wavefunction

- Each basis state or basis ‘ket’ is just like a vector
- The basis vectors for 3D space are the x, y and z axes:

$$|x\rangle, |y\rangle, |z\rangle$$

- They are orthogonal, like the basis states
- Any point (state) within 3D space can be composed of these basis states:

$$U = a|x\rangle + b|y\rangle + \mathrm{c}|z\rangle$$

- Similarly for our Wavefunction:

$$\overrightarrow{\Psi} = \sum_{i}^{dim} c_i |m_L, m_S\rangle_i$$

The Wavefunction

» The action of the Hamiltonian on these basis states mixes them together

» We find a solution for the mixed states that satisfy the Schrödinger equation

» This is done by evaluating the matrix representation of the Hamiltonian and diagonalizing it to find the solution

» The diagonalization procedure necessarily finds eigenvectors that are orthogonal

» That is, the mixtures of the basis states are also orthogonal; therefore the action of the Hamiltonian is simply a rotation!

» This is the foundation of Matrix Mechanics

The Wavefunction

» The matrix representation of the Hamiltonian spans the Hilbert space of the problem

$|-3,-1\rangle \quad |-3,0\rangle \quad |-3,1\rangle \quad |-2,-1\rangle \quad |-2,0\rangle \quad |-2,1\rangle \quad |-1,-1\rangle \quad |-1,0\rangle \quad |-1,1\rangle \quad |0,-1\rangle \quad |0,0\rangle \quad |0,1\rangle \quad |1,-1\rangle \quad |1,0\rangle \quad |1,1\rangle \quad |2,-1\rangle$

$\langle -3,-1|$

$\langle -3,0|$

$\langle -3,1|$

$\langle -2,-1|$

$\langle -2,0|$

$\langle -2,1|$

$\langle -1,-1|$

$\langle -1,0|$

$$\square = \langle -3,-1|\hat{H}|-3,-1\rangle$$

$$\square = \langle -3,0|\hat{H}|-1,1\rangle$$

$$= \langle -1,-1|\hat{H}|-2,-1\rangle$$

$$\square$$

The Wavefunction

» So what is

$$\langle m'_L, m'_S|\hat{H}|m_L, m_S\rangle$$

» It is a matrix element; just a number

» It is determined by the Hamiltonian operating on the basis ket, followed by the inner product with the bra

The Wavefunction

Angular Momentum

» While spin and orbital angular momentum are fundamentally different, they obey the same rules

» Operators act on angular momentum states

» States that are not altered by the operator are eigenstates of that operator

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

Angular Momentum

» Determining the matrix elements of simple operators is straight forward

$$\langle m_L', m_S' | \hat{S}_z | m_L, m_S \rangle$$
$$= m_S \langle m_L', m_S' || m_L, m_S \rangle$$
$$= m_S \delta_{m_L', m_L} \delta_{m_S', m_S}$$

» The Kronecker delta is equal to one if the two variables are the same, otherwise it is zero

» So this element equals m_S if $m_S{}' = m_S$ and if $m_L{}' = m_L$, otherwise it equals 0.

» Operators only act on the part of the function they represent

$$\hat{S}_z|m_L, m_S\rangle \equiv I|m_L\rangle \otimes \hat{S}_z|m_S\rangle$$

» Or

$$\hat{S}_{1_z}\hat{S}_{2_x}\left|m_{S_1}, m_{S_2}\right\rangle \equiv \hat{S}_{1_z}\left|m_{S_1}\right\rangle \otimes \hat{S}_{2_x}\left|m_{S_2}\right\rangle$$

» Think of them as independent ‘spaces’

» We just write them together for convenience

» Our Hamiltonian contains terms like

$$\vec{\hat{L}} \cdot \vec{\hat{S}}$$

» The dot product expands to read

$$\vec{\hat{L}} \cdot \vec{\hat{S}} = \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z$$

$$\vec{\hat{L}} \cdot \vec{\hat{S}} = \frac{1}{2}\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right) + \hat{L}_z\hat{S}_z$$

» The operators are then applied as shown previously

» Thus, the matrix elements of the term

$$\vec{\hat{L}} \cdot \vec{\hat{S}}$$

» Are easily evaluated as

$$\left\langle m_L{}', m_S{}' \right| \left[\frac{1}{2}\left(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+\right) + \hat{L}_z\hat{S}_z \right] \left| m_L, m_S \right\rangle$$

$$= \frac{1}{2}\left\langle m_L{}', m_S{}' \middle| \hat{L}_+\hat{S}_- \middle| m_L, m_S \right\rangle + \frac{1}{2}\left\langle m_L{}', m_S{}' \middle| \hat{L}_-\hat{S}_+ \middle| m_L, m_S \right\rangle + \left\langle m_L{}', m_S{}' \middle| \hat{L}_z\hat{S}_z \middle| m_L, m_S \right\rangle$$

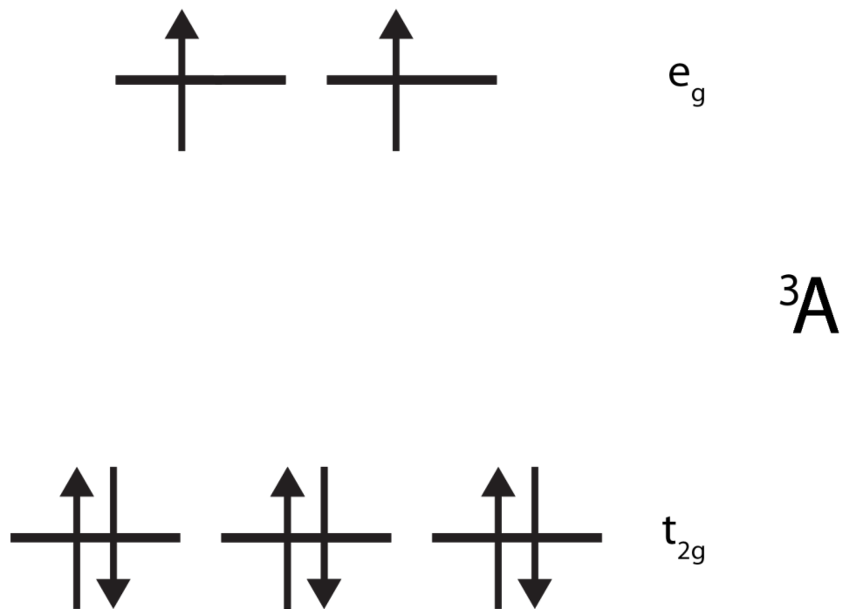
$$= \frac{1}{2}\sqrt{S(S+1) - m_S(m_S - 1)}\sqrt{L(L+1) - m_L(m_L + 1)}\,\delta_{m_L{}', m_L+1}\,\delta_{m_S{}', m_S-1}$$

$$+ \frac{1}{2}\sqrt{S(S+1) - m_S(m_S + 1)}\sqrt{L(L+1) - m_L(m_L - 1)}\,\delta_{m_L{}', m_L-1}\,\delta_{m_S{}', m_S+1}$$

$$+ m_S m_L \delta_{m_L{}', m_L}\,\delta_{m_S{}', m_S}$$

Angular Momentum

- OK, so how about an example…
- Consider a single octahedral Ni(II) ion



- No orbital degeneracy, S = 1

» We would like to examine an axial zero field splitting

$$\hat{H} = D\left(\hat{S}_z^2 - \frac{1}{3}S(S+1)\right)$$

» So what are our basis states?

$$|m_S\,\rangle \equiv \left|Ni^{II}, 3d^8,\ {}^3A, 1, m_S\right\rangle$$

» Remember, $m_S = -S, -S+1, \dots, S-1, S$

$$m_S = -1{,}0{,}1$$

» And what does our matrix look like?

Angular Momentum

» The Hamiltonian matrix

$$\begin{bmatrix} \langle 1|\hat{H}|1\rangle & \langle 1|\hat{H}|0\rangle & \langle 1|\hat{H}|-1\rangle \\ \langle 0|\hat{H}|1\rangle & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|-1\rangle \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

» Our matrix elements all have the form

$$\left\langle m_S' \middle| \left[D\left(\hat{S}_z^2 - \frac{1}{3}S(S+1) \right) \right] \middle| m_S \right\rangle$$

» And are easily evaluated…

$$= D\left\langle m_S' \middle| \hat{S}_z^2 \middle| m_S \right\rangle + D\left(-\frac{1}{3}S(S+1) \right)\langle m_S' | m_S \rangle$$

$$= D m_S m_S \delta_{m_S', m_S} + D\left(-\frac{1}{3}S(S+1) \right)\delta_{m_S', m_S}$$

$$= D\left(m_S m_S - \frac{1}{3}S(S+1) \right)\delta_{m_S', m_S}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \langle 1|\hat{H}|1\rangle & \langle 1|\hat{H}|0\rangle & \langle 1|\hat{H}|-1\rangle \\ \langle 0|\hat{H}|1\rangle & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|-1\rangle \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & \langle 1|\widehat{H}|0\rangle & \langle 1|\widehat{H}|-1\rangle \\ \langle 0|\widehat{H}|1\rangle & \langle 0|\widehat{H}|0\rangle & \langle 0|\widehat{H}|-1\rangle \\ \langle -1|\widehat{H}|1\rangle & \langle -1|\widehat{H}|0\rangle & \langle -1|\widehat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & \langle 1|\hat{H}|-1\rangle \\ \langle 0|\hat{H}|1\rangle & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|-1\rangle \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ \langle 0|\hat{H}|1\rangle & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|-1\rangle \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ 0 & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|-1\rangle \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ 0 & -\frac{2D}{3} & \langle 0|\hat{H}|-1\rangle \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S{}',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ 0 & -\frac{2D}{3} & 0 \\ \langle -1|\hat{H}|1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ 0 & -\frac{2D}{3} & 0 \\ 0 & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

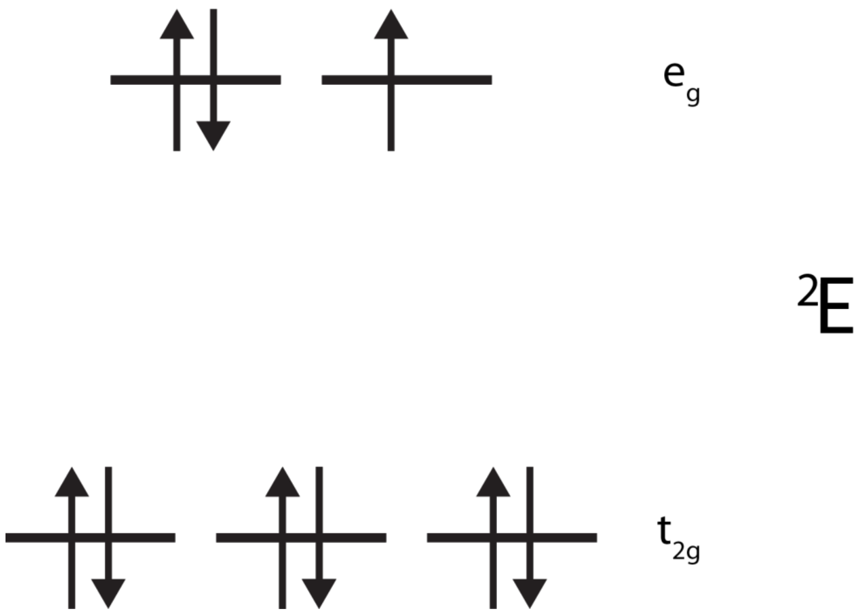
$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ 0 & -\frac{2D}{3} & 0 \\ 0 & 0 & \langle -1|\hat{H}|-1\rangle \end{bmatrix}$$

$$= D\left(m_S m_S - \frac{2}{3}\right)\delta_{m_S',m_S}$$

$$\begin{bmatrix} \frac{D}{3} & 0 & 0 \\ 0 & -\frac{2D}{3} & 0 \\ 0 & 0 & \frac{D}{3} \end{bmatrix}$$

» How about another example?

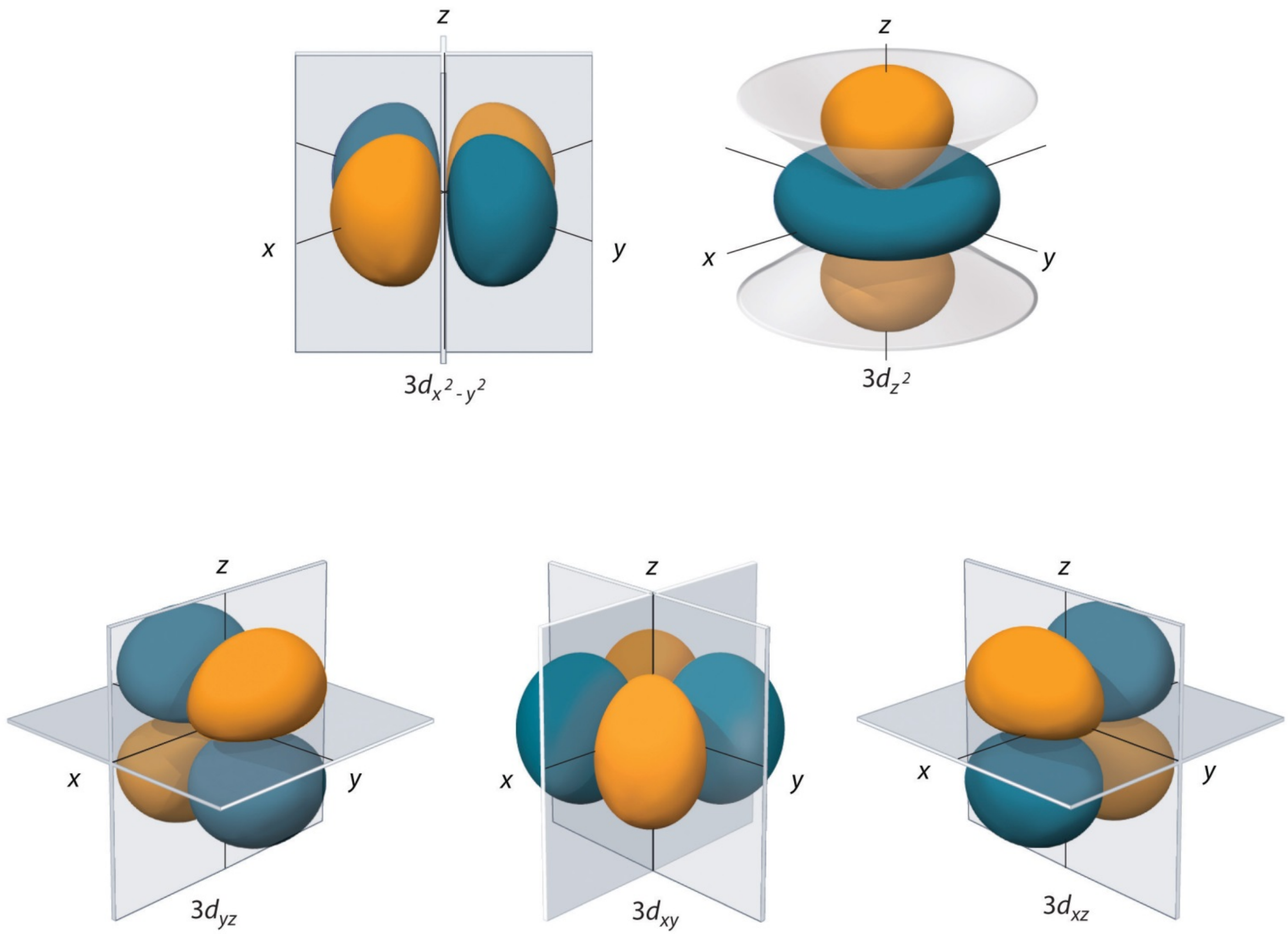
» Consider a dimer of octahedral Cu(II) ions



» No orbital moment in octahedral E terms, $S = {}^1/_2$

Angular Momentum

» Think about the e_g orbitals:



3d Crystal Fields

» We would like to examine the exchange interaction

$$\hat{H} = -2J\vec{\hat{S}}_1 \cdot \vec{\hat{S}}_2$$

» So what are our basis states?

$$|m_{S_1}, m_{S_2}\rangle \equiv \left|Cu^{II}{}_1, 3d^9, \ {}^2E, \frac{1}{2}, m_{S_1}\right\rangle \otimes \left|Cu^{II}{}_2, 3d^9, \ {}^2E, \frac{1}{2}, m_{S_2}\right\rangle$$

» Remember, $m_S = -S, -S+1, \ldots, S-1, S$

$$m_S = -\frac{1}{2}, \frac{1}{2}$$

» And what does our matrix look like?

» The Hamiltonian matrix

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

» We need the matrix elements, so let's expand our operator…

$$-2J\vec{\hat{S}}_1 \cdot \vec{\hat{S}}_2 = -2J(\hat{S}_{1_x}\hat{S}_{2_x} + \hat{S}_{1_y}\hat{S}_{2_y} + \hat{S}_{1_z}\hat{S}_{2_z})$$

$$-2J\vec{\hat{S}}_1 \cdot \vec{\hat{S}}_2 = -2J\left(\frac{1}{2}(\hat{S}_{1_+}\hat{S}_{2_-} + \hat{S}_{1_-}\hat{S}_{2_+}) + \hat{S}_{1_z}\hat{S}_{2_z}\right)$$

» Therefore our matrix elements have the form

$$\left\langle m_{S_1}', m_{S_2}'\right| \left[-2J\left(\frac{1}{2}(\hat{S}_{1_+}\hat{S}_{2_-} + \hat{S}_{1_-}\hat{S}_{2_+}) + \hat{S}_{1_z}\hat{S}_{2_z}\right)\right] \left|m_{S_1}, m_{S_2}\right\rangle$$

» These are easily evaluated as before

$$\left\langle m_{S_1}', m_{S_2}' \right| \left[-2J \left(\frac{1}{2} \left(\hat{S}_{1_+} \hat{S}_{2_-} + \hat{S}_{1_-} \hat{S}_{2_+} \right) + \hat{S}_{1_z} \hat{S}_{2_z} \right) \right] \left| m_{S_1}, m_{S_2} \right\rangle$$

$$= -2J \left(\begin{gathered} \frac{1}{2} \langle m_{S_1}', m_{S_2}' | \hat{S}_{1_+} \hat{S}_{2_-} | m_{S_1}, m_{S_2} \rangle + \frac{1}{2} \langle m_{S_1}', m_{S_2}' | \hat{S}_{1_-} \hat{S}_{2_+} | m_{S_1}, m_{S_2} \rangle \\ + \langle m_{S_1}', m_{S_2}' | \hat{S}_{1_z} \hat{S}_{2_z} | m_{S_1}, m_{S_2} \rangle \end{gathered} \right)$$

$$= -2J \left(\begin{gathered} \frac{1}{2} \sqrt{S_1(S_1+1) - m_{S_1}(m_{S_1}+1)} \sqrt{S_2(S_2+1) - m_{S_2}(m_{S_2}-1)}\, \delta_{m_{S_1}', m_{S_1}+1} \delta_{m_{S_2}', m_{S_2}-1} \\ + \frac{1}{2} \sqrt{S_1(S_1+1) - m_{S_1}(m_{S_1}-1)} \sqrt{S_2(S_2+1) - m_{S_2}(m_{S_2}+1)}\, \delta_{m_{S_1}', m_{S_1}-1} \delta_{m_{S_2}', m_{S_2}+1} \\ + m_{S_1} m_{S_2} \delta_{m_{S_1}', m_{S_1}} \delta_{m_{S_2}', m_{S_2}} \end{gathered} \right)$$

So what is this element?

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

Angular Momentum

$$\left\langle \frac{1}{2}, \frac{1}{2} \right| \left[-2J \left(\frac{1}{2} \left(\hat{S}_{1_+} \hat{S}_{2_-} + \hat{S}_{1_-} \hat{S}_{2_+} \right) + \hat{S}_{1_z} \hat{S}_{2_z} \right) \right] \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

» $m_{S_1} = m_{S_2} = m_{S_1}{}' = m_{S_2}{}' = \frac{1}{2}$

$$= -2J \left(\begin{array}{c} \frac{1}{2} \sqrt{S_1(S_1+1) - m_{S_1}(m_{S_1}+1)} \sqrt{S_2(S_2+1) - m_{S_2}(m_{S_2}-1)}\, \delta_{m_{S_1}{}', m_{S_1}+1} \delta_{m_{S_2}{}', m_{S_2}-1} \\ + \frac{1}{2} \sqrt{S_1(S_1+1) - m_{S_1}(m_{S_1}-1)} \sqrt{S_2(S_2+1) - m_{S_2}(m_{S_2}+1)}\, \delta_{m_{S_1}{}', m_{S_1}-1} \delta_{m_{S_2}{}', m_{S_2}+1} \\ + m_{S_1} m_{S_2} \delta_{m_{S_1}{}', m_{S_1}} \delta_{m_{S_2}{}', m_{S_2}} \end{array} \right)$$

$$\left\langle \frac{1}{2}, \frac{1}{2} \right| \left[-2J \left(\frac{1}{2} \left(\hat{S}_{1_+} \hat{S}_{2_-} + \hat{S}_{1_-} \hat{S}_{2_+} \right) + \hat{S}_{1_z} \hat{S}_{2_z} \right) \right] \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$

» $m_{S_1} = m_{S_2} = m_{S_1}{}' = m_{S_2}{}' = \frac{1}{2}$

$$= -2J \left(\begin{array}{c} \frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - m_{S_1}\left(m_{S_1}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - m_{S_2}\left(m_{S_2}-1\right)}\delta_{m_{S_1}{}',m_{S_1}+1}\delta_{m_{S_2}{}',m_{S_2}-1} \\ +\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - m_{S_1}\left(m_{S_1}-1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right) - m_{S_2}\left(m_{S_2}+1\right)}\delta_{m_{S_1}{}',m_{S_1}-1}\delta_{m_{S_2}{}',m_{S_2}+1} \\ +m_{S_1} m_{S_2} \delta_{m_{S_1}{}',m_{S_1}} \delta_{m_{S_2}{}',m_{S_2}} \end{array} \right)$$

$$\left\langle \frac{1}{2},\frac{1}{2}\right|\left[-2J\left(\frac{1}{2}\left(\hat{S}_{1_+}\hat{S}_{2_-}+\hat{S}_{1_-}\hat{S}_{2_+}\right)+\hat{S}_{1_z}\hat{S}_{2_z}\right)\right]\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

» $m_{S_1} = m_{S_2} = m_{S_1}{}' = m_{S_2}{}' = \frac{1}{2}$

$$= -2J\left(\begin{array}{c} \frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\,\delta_{m_{S_1}{}',m_{S_1}+1}\delta_{m_{S_2}{}',m_{S_2}-1} \\ +\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\delta_{m_{S_1}{}',m_{S_1}-1}\delta_{m_{S_2}{}',m_{S_2}+1} \\ +\frac{1}{2}\times\frac{1}{2}\,\delta_{m_{S_1}{}',m_{S_1}}\delta_{m_{S_2}{}',m_{S_2}} \end{array}\right)$$

$$\left\langle\frac{1}{2},\frac{1}{2}\right|\left[-2J\left(\frac{1}{2}\left(\hat{S}_{1_+}\hat{S}_{2_-}+\hat{S}_{1_-}\hat{S}_{2_+}\right)+\hat{S}_{1_z}\hat{S}_{2_z}\right)\right]\left|\frac{1}{2},\frac{1}{2}\right\rangle$$

» $m_{S_1} = m_{S_2} = m_{S_1}{}' = m_{S_2}{}' = \frac{1}{2}$

$$= -2J\left(\begin{array}{c} \frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\,0\times 0 \\ +\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\,0\times 0 \\ +\frac{1}{2}\times\frac{1}{2}\times 1\times 1 \end{array}\right)$$

$$= -2J\left(\frac{1}{4}\right) = -\frac{J}{2}$$

What about this one?

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

$$\left\langle -\frac{1}{2},\frac{1}{2}\right|\left[-2J\left(\frac{1}{2}\left(\hat{S}_{1_+}\hat{S}_{2_-}+\hat{S}_{1_-}\hat{S}_{2_+}\right)+\hat{S}_{1_z}\hat{S}_{2_z}\right)\right]\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

» $m_{S_1} = m_{S_2}{}' = \frac{1}{2}, m_{S_2} = m_{S_1}{}' = -\frac{1}{2}$

$$= -2J\left(\begin{array}{c} \frac{1}{2}\sqrt{S_1(S_1+1)-m_{S_1}(m_{S_1}+1)}\sqrt{S_2(S_2+1)-m_{S_2}(m_{S_2}-1)}\,\delta_{m_{S_1}{}',m_{S_1}+1}\delta_{m_{S_2}{}',m_{S_2}-1} \\ +\frac{1}{2}\sqrt{S_1(S_1+1)-m_{S_1}(m_{S_1}-1)}\sqrt{S_2(S_2+1)-m_{S_2}(m_{S_2}+1)}\,\delta_{m_{S_1}{}',m_{S_1}-1}\delta_{m_{S_2}{}',m_{S_2}+1} \\ +m_{S_1}m_{S_2}\delta_{m_{S_1}{}',m_{S_1}}\delta_{m_{S_2}{}',m_{S_2}} \end{array}\right)$$

$$\left\langle -\frac{1}{2},\frac{1}{2}\right|\left[-2J\left(\frac{1}{2}\left(\hat{S}_{1_+}\hat{S}_{2_-}+\hat{S}_{1_-}\hat{S}_{2_+}\right)+\hat{S}_{1_z}\hat{S}_{2_z}\right)\right]\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

» $m_{S_1} = m_{S_2}{}' = \frac{1}{2}, m_{S_2} = m_{S_1}{}' = -\frac{1}{2}$

$$= -2J\left(\begin{array}{c}\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-m_{S_1}\left(m_{S_1}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-m_{S_2}\left(m_{S_2}-1\right)}\delta_{m_{S_1}{}',m_{S_1}+1}\delta_{m_{S_2}{}',m_{S_2}-1}\\ +\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-m_{S_1}\left(m_{S_1}-1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-m_{S_2}\left(m_{S_2}+1\right)}\delta_{m_{S_1}{}',m_{S_1}-1}\delta_{m_{S_2}{}',m_{S_2}+1}\\ +m_{S_1}m_{S_2}\delta_{m_{S_1}{}',m_{S_1}}\delta_{m_{S_2}{}',m_{S_2}}\end{array}\right)$$

$$\left\langle -\frac{1}{2},\frac{1}{2}\right|\left[-2J\left(\frac{1}{2}\left(\hat{S}_{1_+}\hat{S}_{2_-}+\hat{S}_{1_-}\hat{S}_{2_+}\right)+\hat{S}_{1_z}\hat{S}_{2_z}\right)\right]\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

» $m_{S_1} = m_{S_2}{}' = \frac{1}{2}, m_{S_2} = m_{S_1}{}' = -\frac{1}{2}$

$$= -2J\left(\begin{array}{c} \frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(\left(-\frac{1}{2}\right)-1\right)}\delta_{m_{S_1}',m_{S_1}+1}\delta_{m_{S_2}',m_{S_2}-1} \\ +\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(\left(-\frac{1}{2}\right)-1\right)}\delta_{m_{S_1}',m_{S_1}-1}\delta_{m_{S_2}',m_{S_2}+1} \\ +\frac{1}{2}\left(-\frac{1}{2}\right)\delta_{m_{S_1}',m_{S_1}}\delta_{m_{S_2}',m_{S_2}} \end{array}\right)$$

$$\left\langle -\frac{1}{2},\frac{1}{2}\right|\left[-2J\left(\frac{1}{2}\left(\hat{S}_{1_+}\hat{S}_{2_-}+\hat{S}_{1_-}\hat{S}_{2_+}\right)+\hat{S}_{1_z}\hat{S}_{2_z}\right)\right]\left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

» $m_{S_1} = m_{S_2}{}' = \frac{1}{2}, m_{S_2} = m_{S_1}{}' = -\frac{1}{2}$

$$= -2J\left(\begin{array}{c} \frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(\left(-\frac{1}{2}\right)-1\right)}\,0\times0 \\ +\frac{1}{2}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(\left(-\frac{1}{2}\right)-1\right)}\,1\times1 \\ +\frac{1}{2}\left(-\frac{1}{2}\right)\times0\times0 \end{array}\right)$$

$$= -2J\left(\frac{1}{2}\sqrt{\frac{3}{4}+\frac{1}{4}}\sqrt{\frac{3}{4}+\frac{1}{4}}\right)$$

$$= -J$$

Angular Momentum

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

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & \left\langle \frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle \\
\left\langle \frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle \frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle \\
\left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & -J & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle \\
\left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & \left\langle \frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & -J & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle
\end{bmatrix}
$$

Angular Momentum

$$\begin{bmatrix} -\frac{J}{2} & 0 & 0 & 0 \\ \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\ \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & -J & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\ \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \end{bmatrix}$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & -J & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & -J & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle
\end{bmatrix}
$$

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & -J & \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & -J & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, \frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \\
\left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & -J & 0 \\
\left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & -J & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle \\
\left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & -J & 0 \\
0 & -J & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle \\
\left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & -J & 0 \\
0 & -J & \frac{J}{2} & \left\langle -\frac{1}{2},\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle \\
\left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2},-\frac{1}{2}\middle|\hat{H}\middle|-\frac{1}{2},-\frac{1}{2}\right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & -J & 0 \\
0 & -J & \frac{J}{2} & 0 \\
\left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle
\end{bmatrix}
$$

Angular Momentum

$$
\begin{bmatrix}
-\frac{J}{2} & 0 & 0 & 0 \\
0 & \frac{J}{2} & -J & 0 \\
0 & -J & \frac{J}{2} & 0 \\
0 & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| \frac{1}{2}, -\frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle
\end{bmatrix}
$$

Angular Momentum

$$\begin{bmatrix} -\frac{J}{2} & 0 & 0 & 0 \\ 0 & \frac{J}{2} & -J & 0 \\ 0 & -J & \frac{J}{2} & 0 \\ 0 & 0 & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, \frac{1}{2} \right\rangle & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \end{bmatrix}$$

Angular Momentum

$$\begin{bmatrix} -\frac{J}{2} & 0 & 0 & 0 \\ 0 & \frac{J}{2} & -J & 0 \\ 0 & -J & \frac{J}{2} & 0 \\ 0 & 0 & 0 & \left\langle -\frac{1}{2}, -\frac{1}{2} \middle| \hat{H} \middle| -\frac{1}{2}, -\frac{1}{2} \right\rangle \end{bmatrix}$$

Angular Momentum

$$\begin{bmatrix} -\frac{J}{2} & 0 & 0 & 0 \\ 0 & \frac{J}{2} & -J & 0 \\ 0 & -J & \frac{J}{2} & 0 \\ 0 & 0 & 0 & -\frac{J}{2} \end{bmatrix}$$

Angular Momentum

$$\boxed{\begin{matrix} \frac{J}{2} & -J \\ -J & \frac{J}{2} \end{matrix}}$$

» Eigenvalues and eigenvectors are:

$$-\frac{J}{2}, \quad \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},-\frac{1}{2}\right\rangle+\left|-\frac{1}{2},\frac{1}{2}\right\rangle\right) \qquad \frac{3J}{2}, \quad \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},-\frac{1}{2}\right\rangle-\left|-\frac{1}{2},\frac{1}{2}\right\rangle\right)$$

» Therefore, we have three states at $\mathrm{E}=-\frac{J}{2}$ (triplet)

» And one state at $\mathrm{E}=\frac{3J}{2}$ (singlet)

Angular Momentum

Linear Algebra

» The process of diagonalizing the Hamiltonian is tricky, but the idea is simple

» Any real symmetric or complex hermitian matrix (*A*) can be brought to a diagonal form by an invertible matrix (*P*)

$$A = PDP^{-1}$$

» The diagonal values of *D* are the eigenvalues (energies) of the system, while the columns of *P* specify the mixtures of the basis states that comprise the eigenvectors (wavefunctions)

» Can be done for small matrices analytically, but we usually use computers to do this numerically!

Linear Algebra

Magnetic properties

- From diagonalization of the Hamiltonian matrix we get:
  - Eigenvalues (state energies)
  - Eigenvectors (state vectors / wavefunctions)

- Fundamental relationships:

$$M \propto -\frac{\partial E}{\partial B}$$

$$\chi \propto \frac{\partial M}{\partial B}$$

Magnetic Properties

» Magnetization

Brief stat. mech. Reminder:

Partition function

$$M \propto -\frac{\partial E}{\partial B}$$

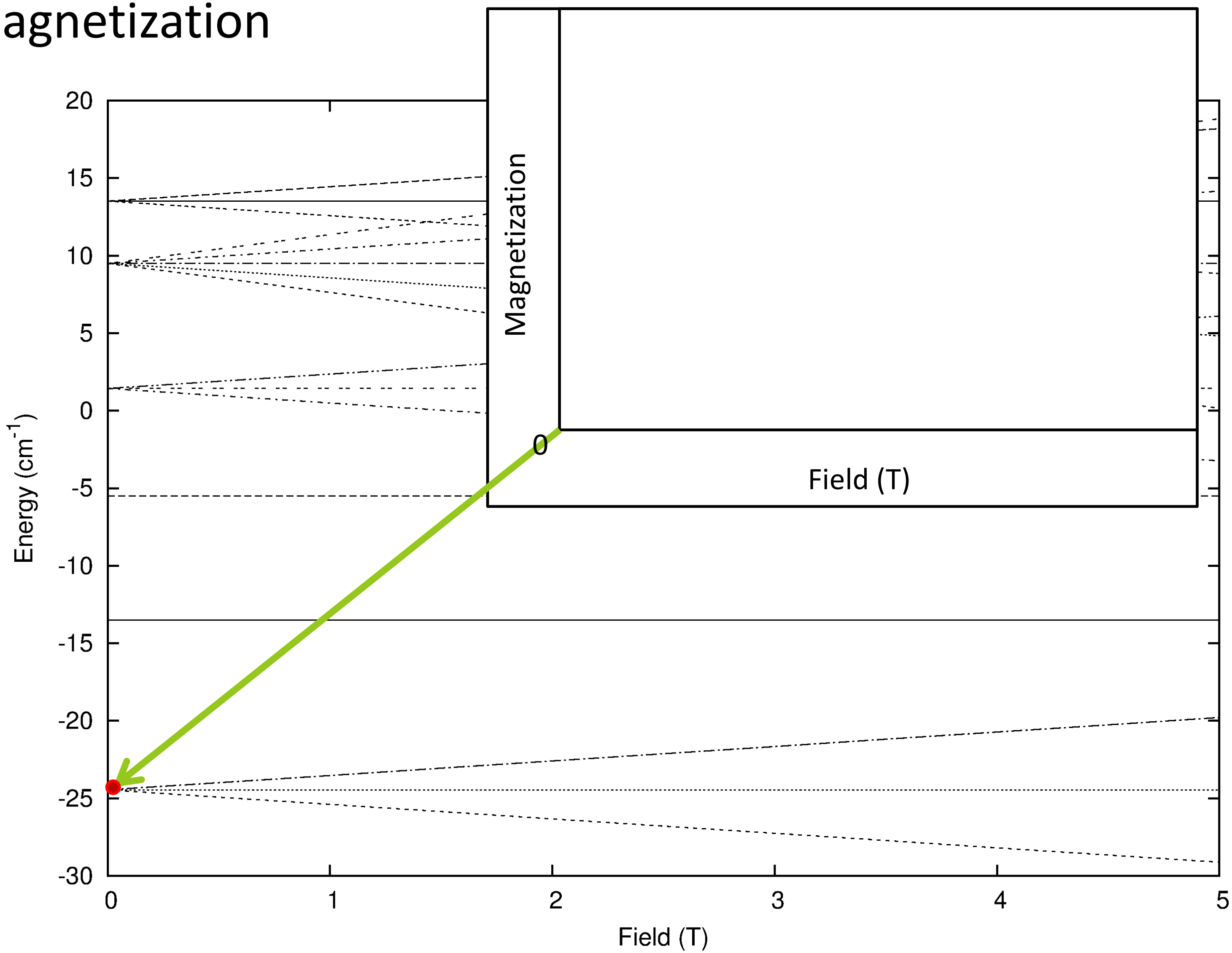
Boltzmann population factor

$$M_\alpha = \frac{1}{Z\mu_B} \sum_{i=1}^{dim} -\frac{\partial E_i}{\partial B_\alpha} e^{\frac{-E_i}{k_B T}}$$

Remember:
Energy levels are functions of the magnetic field!

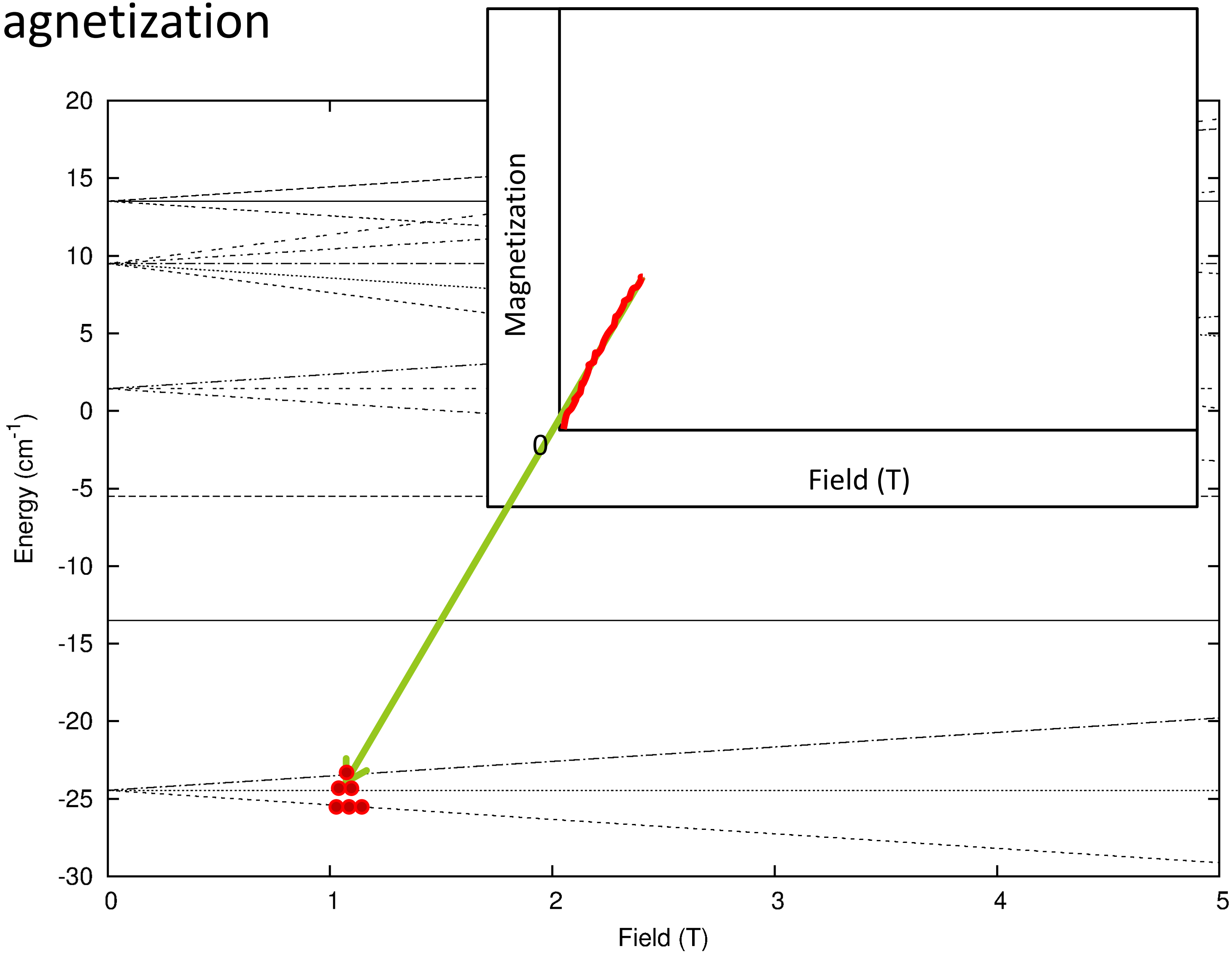
Magnetic Properties

» Magnetization



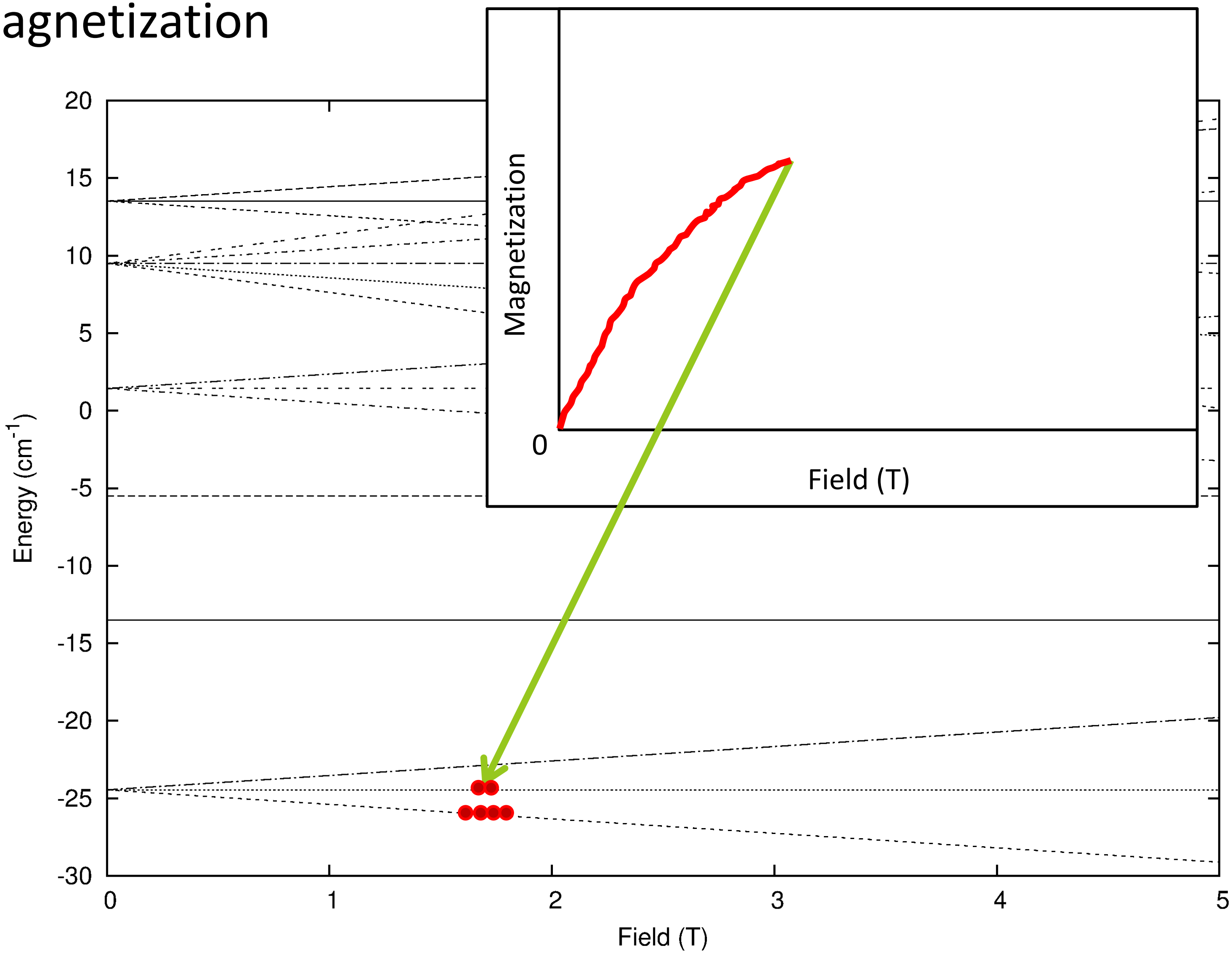
Magnetic Properties

» Magnetization



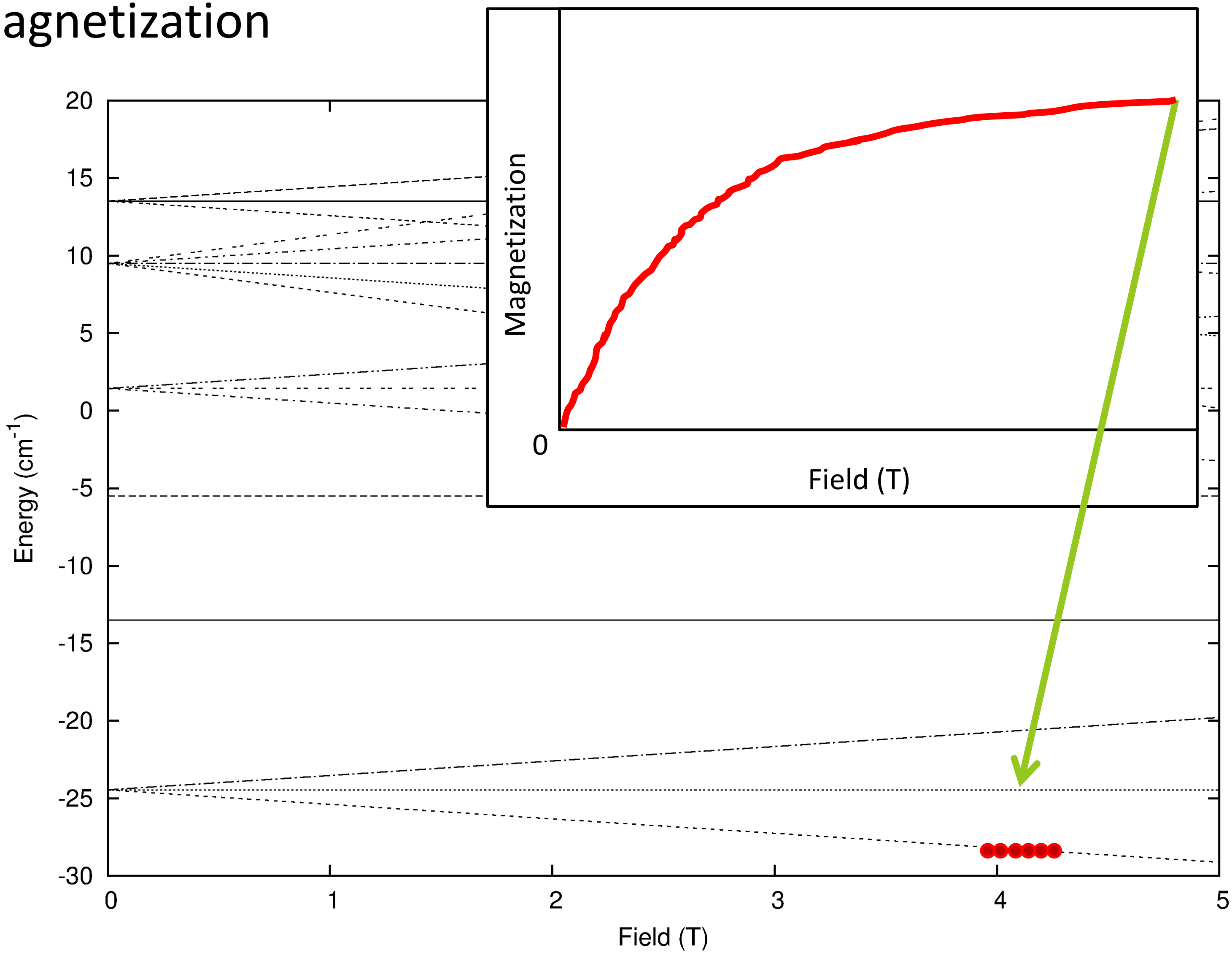
Magnetic Properties

» Magnetization



Magnetic Properties

» Magnetization



Magnetic Properties

$$\chi_{\alpha,\beta} = \frac{\partial M_\alpha}{\partial B_\beta}$$

$$= \frac{N_A}{10k_BTZ^2}\left[Z\left(\sum_{i=1}^{dim}\frac{\partial E_i}{\partial B_\alpha}\frac{\partial E_i}{\partial B_\beta}e^{\frac{-E_i}{k_BT}}\right.\right.$$

$$\left. - k_BT\sum_{i=1}^{dim}\frac{\partial^2 E_i}{\partial B_\alpha \partial B_\beta}e^{\frac{-E_i}{k_BT}}\right)$$

$$\left. - \left(\sum_{i=1}^{dim}\frac{\partial E_i}{\partial B_\alpha}e^{\frac{-E_i}{k_BT}}\right)\left(\sum_{i=1}^{dim}\frac{\partial E_i}{\partial B_\beta}e^{\frac{-E_i}{k_BT}}\right)\right]$$

Magnetic Properties

» Slightly easier to implement…

Dependent on direction of B

$$M_{\alpha} = \frac{k_B T}{\mu_B} \frac{\partial \ln Z}{\partial B_{\alpha}}$$

Dependent on two directions!

$$\chi_{\alpha,\beta} = \frac{N_A k_B T}{10} \frac{\partial^2 \ln Z}{\partial B_{\alpha} \partial B_{\beta}}$$

» Therefore, generally a 3 x 3 tensor $\chi = \begin{bmatrix} \chi_{x,x} & \chi_{x,y} & \chi_{x,z} \\ \chi_{y,x} & \chi_{y,y} & \chi_{y,z} \\ \chi_{z,x} & \chi_{z,y} & \chi_{z,z} \end{bmatrix}$

» Simplifies to a scalar if isotropic

Magnetic Properties

Powder Integration

Powder Averaging

- Isotropic systems:
  - All directions are equivalent
  - Properties need only be evaluated for one direction
- Anisotropic systems:
  - Directions are inequivalent
  - Properties must represent experiment
  - Single crystal or powder experiment

- Susceptibility can be averaged over x, y and z

- Magnetization must be averaged over the hemisphere
  - Due to the inversion symmetry of the magnetic field

Approximations

- Matrix diagonalization is expensive
  - Effort scales $\propto dim^3$

- If anisotropic we must diagonalize a very large number of matrices!

- $dim < 500$, no problem

- $500 < dim < 2000$, can be done with patience

- $dim > 2000$, now that's a boring day…

- Hence, some simplification might be nice!

Approximations

» For isotropic systems ***only***, there is a way…

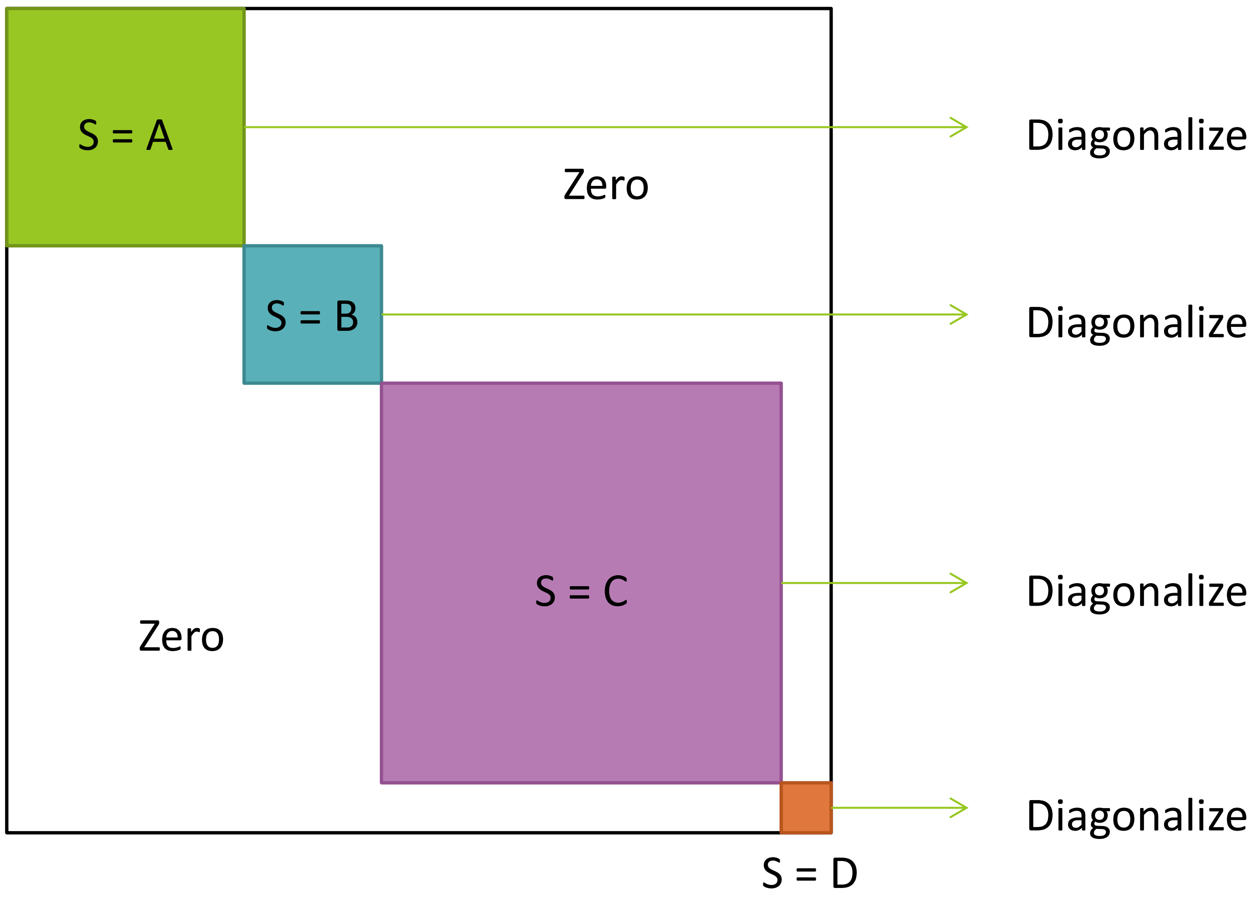
» The isotropic exchange Hamiltonian matrix is block diagonal in a total spin basis!

$$\hat{H}_{iso} = -2 \sum_{i<j}^{i,j \in N} J_{ij} \vec{\hat{S}}_i \cdot \vec{\hat{S}}_j$$

$$\left|S^i, S^j, S^k, m_S{}^i, m_S{}^j, m_S{}^k\right\rangle \rightarrow \left|S^i, S^j, S^k, S_{ij}, S, m_S\right\rangle$$

Approximations

» Matrix now has independent blocks!



» Zeeman Effect treated as a perturbation

Approximations

The Curie Law

» The (empirical) Curie law states:

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

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

» Can we work out C?

» Yes! For perfect paramagnets:

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

The Curie Law

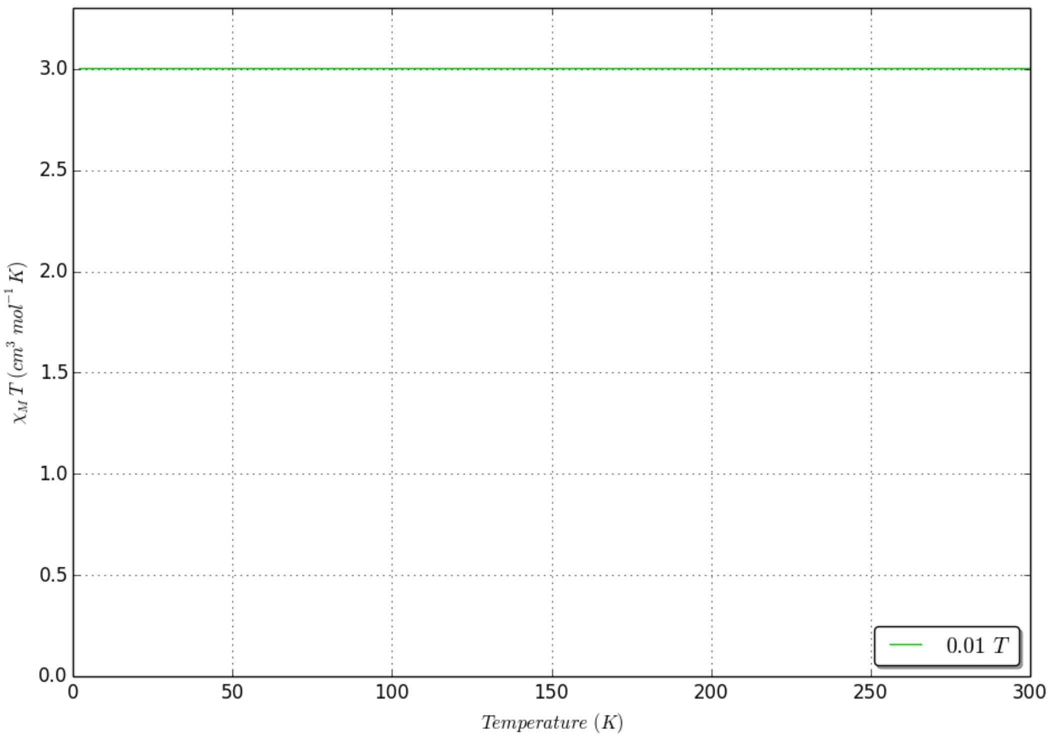
- Rearranging, $\chi T = C$
- Therefore if the Curie Law holds, χT vs. T should be constant
- As temperature is lowered we (usually) see deviations from Curie-like behaviour (this is where the fun happens!)

- A note on units:
  - Chemists usually use $cm^3 mol^{-1} K$ (c.g.s. e.m.u.)
  - Historically also plot $\mu_{eff} \approx 2.828\sqrt{\chi T}$ in units of μ_B

The Curie Law

» A simple S = 2 compound with g = 2:

$$C \approx \frac{g^2}{8} S(S+1) = \frac{4}{8} \times 2 \times (2+1) = \frac{24}{8} = 3\ cm^3 mol^{-1} K$$

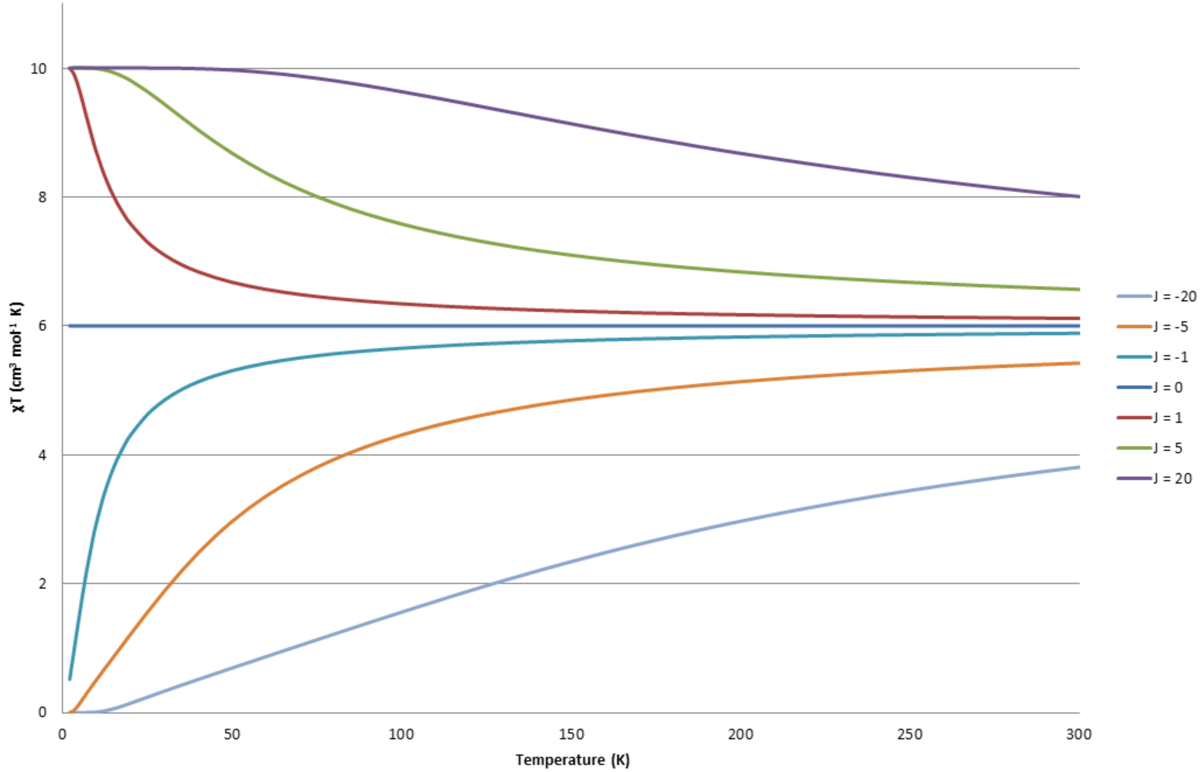


The Curie Law

Exchange coupling

» When spins are coupled the Curie Law will fail (at some point)

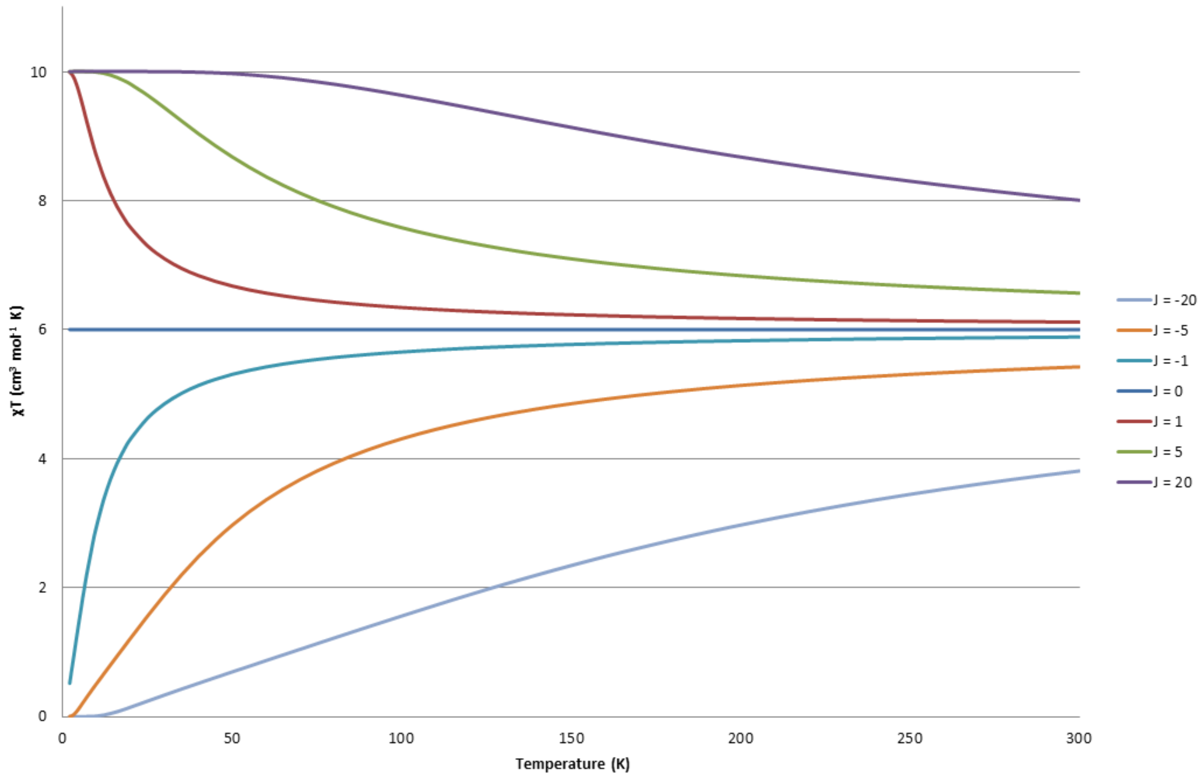
» The strength of the interaction sets the temperature when this happens



Exchange coupling

» If χT saturates at high temperatures, we call this the 'uncoupled moment' (not really uncoupled!!)

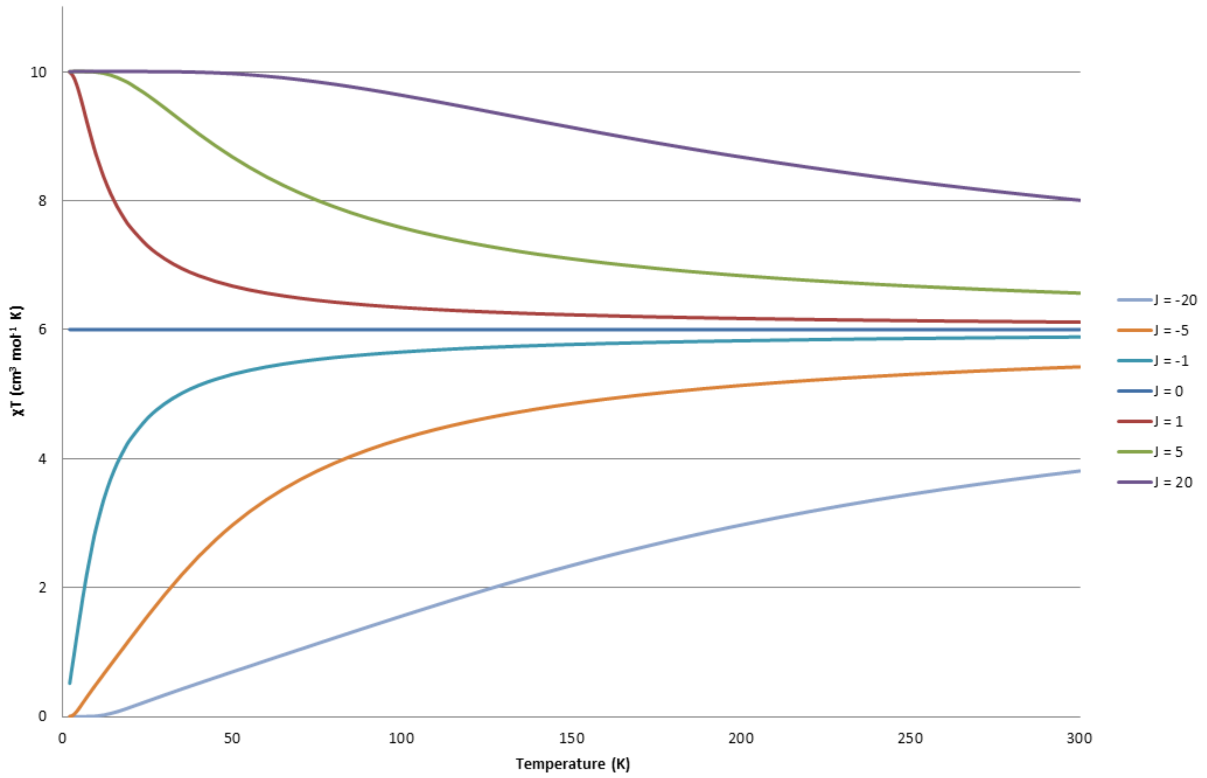
» It is the sum of the Curie contributions of each spin



Exchange coupling

» If χT reduces with temperature, dominant antiferromagnetic

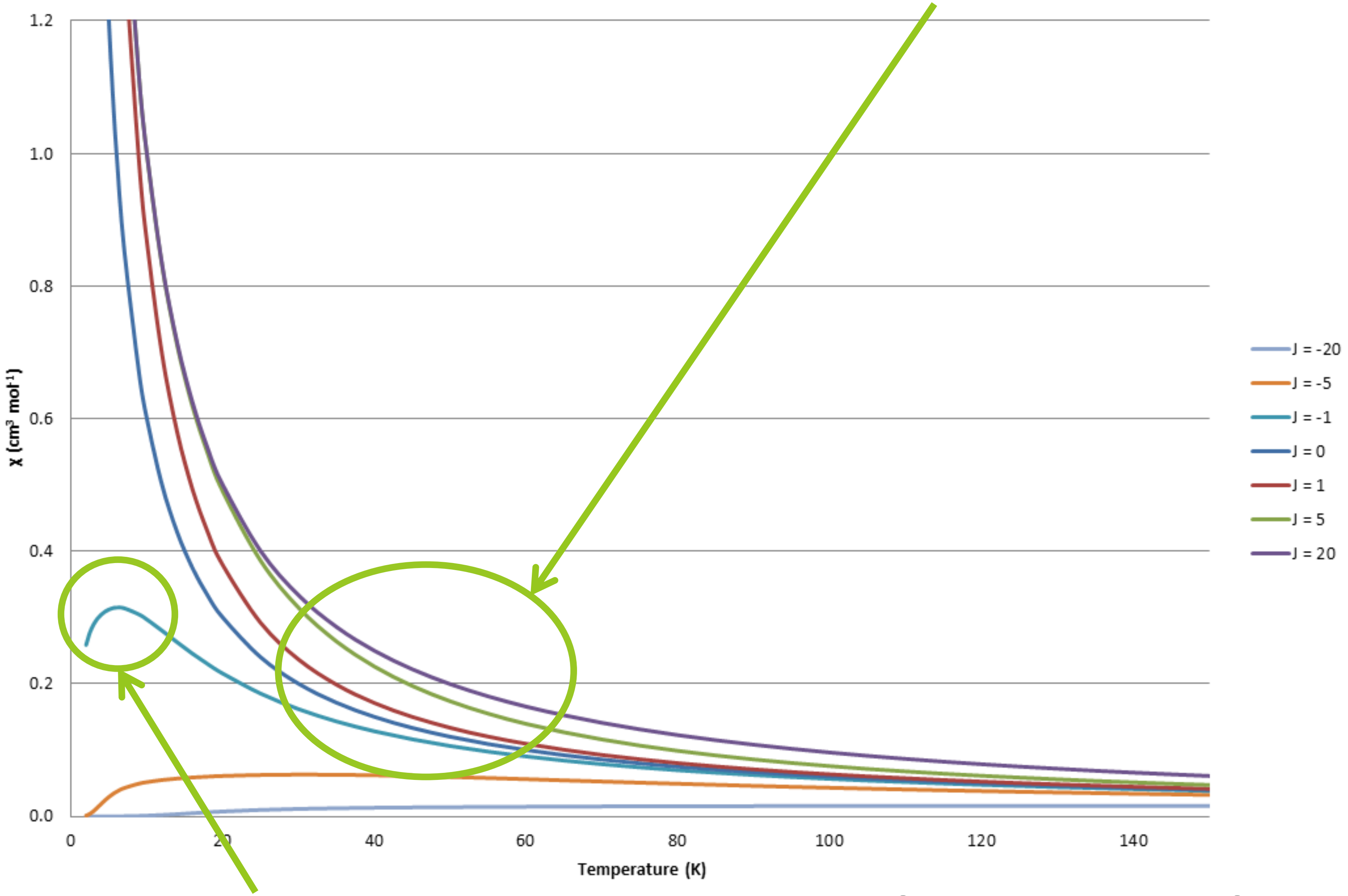
» If χT increases with temperature, dominant ferromagnetic



Exchange coupling

» What about χ?

Ferromagnetic rises faster

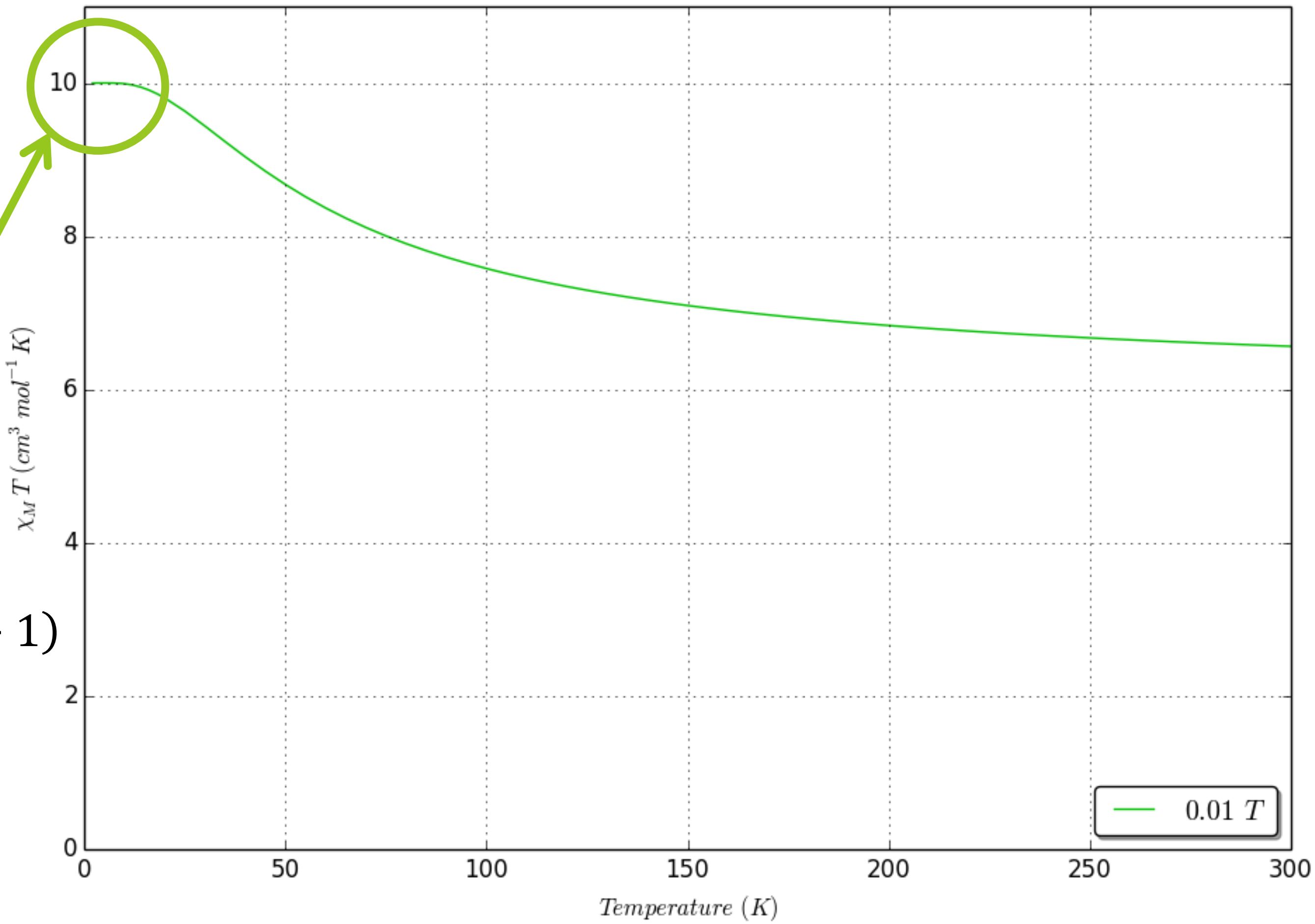


Antiferromagnetic can show a maximum

Exchange coupling

Low temperatures

» At low temperatures, χT can reveal ground spin state



$$\chi T = 10 = \frac{g^2}{8} S(S+1)$$

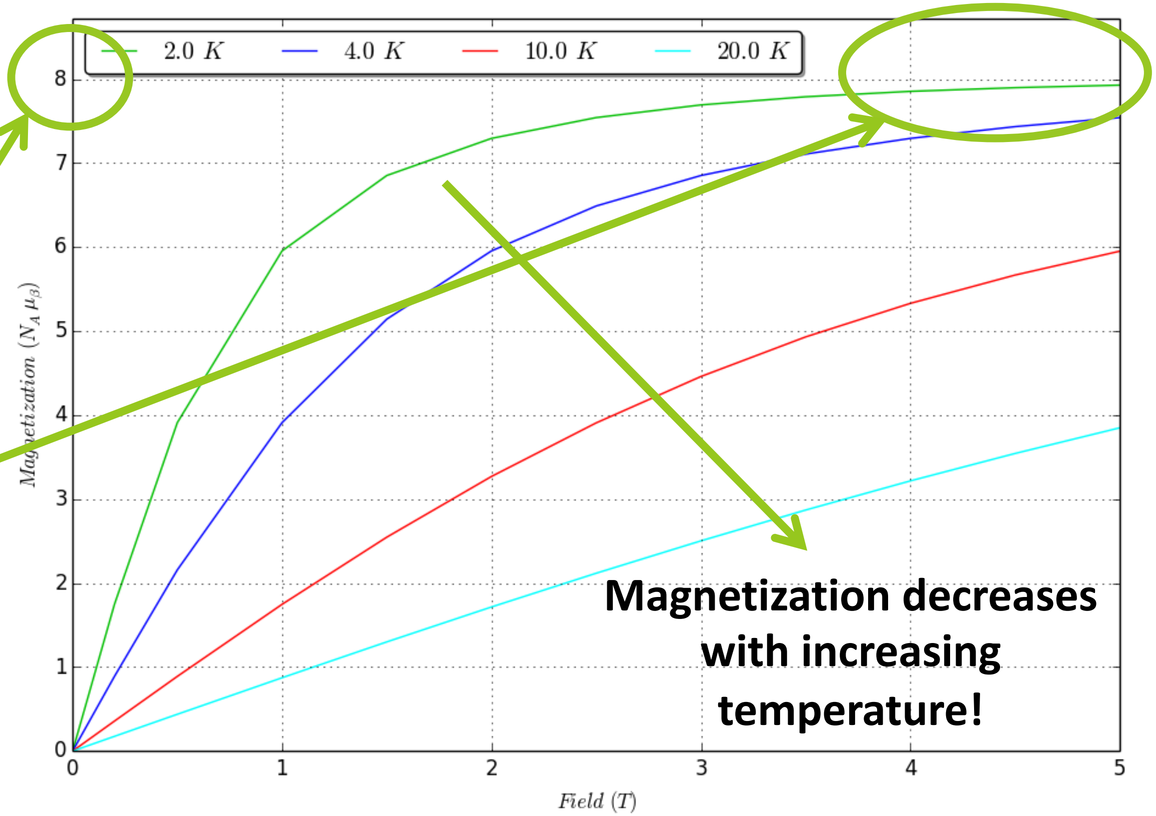
$$20 = S(S+1)$$

$$S = 4$$

Low temperatures

- Magnetization also gives information about the ground spin state
- At the lowest temperature and highest field, magnetization saturates at:

$$M = gS$$



$$M = 8 = gS$$

$$S = 4$$

Low temperatures

The importance of a model

» We are attempting to model a complicated physical reality with a toy model

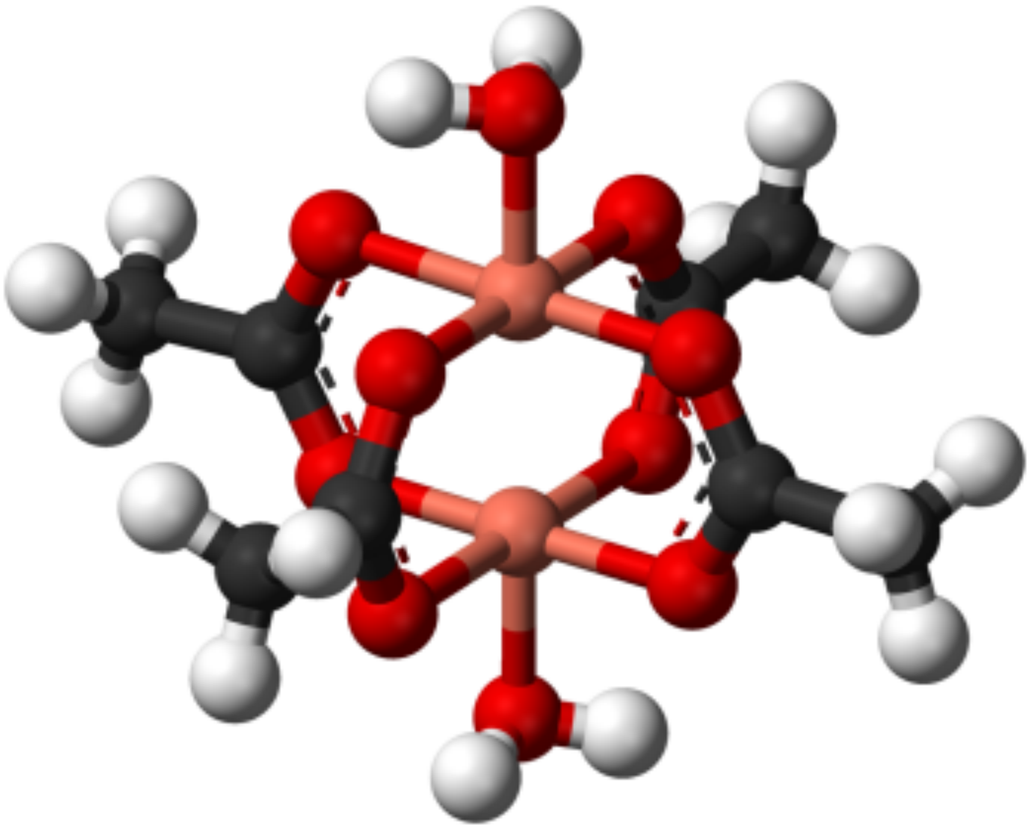
» Remember the simplifications and approximations of the Spin Hamiltonian approach!

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\Psi = E\,\Psi$$

» Always start with the simplest possible model first!

The importance of a model

» When modelling the properties of ANYTHING, always start and finish with the molecule!



The importance of a model

» Draw a sketch of how you design your model

$$Cu^{II}_1 \longrightarrow Cu^{II}_2$$

$$S_1 \xrightarrow{J_1} S_2$$

The importance of a model

» Define the Hamiltonian you will use

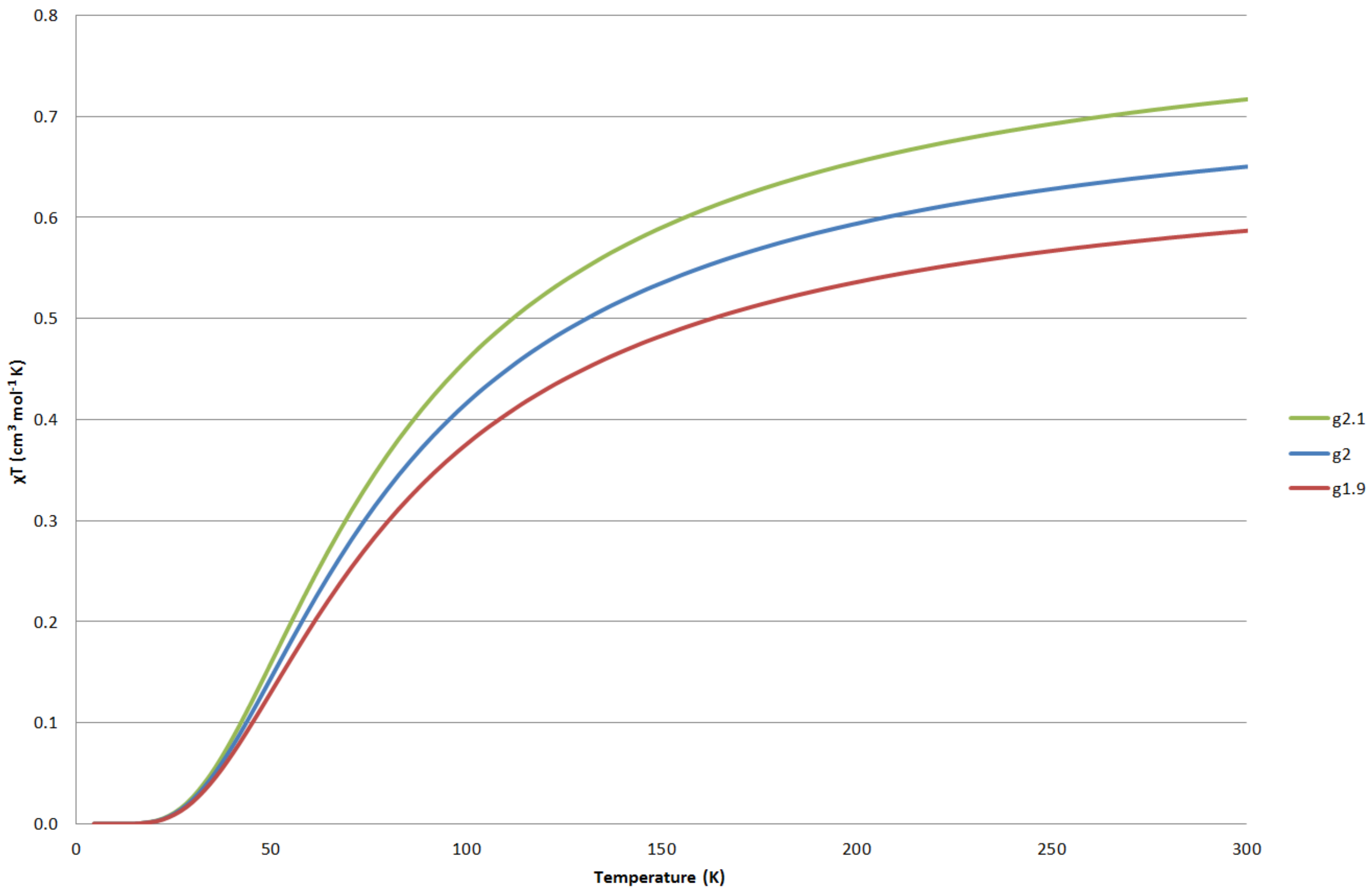
$$\hat{H} = -2J_1\vec{\hat{S}}_1 \cdot \vec{\hat{S}}_2 + \mu_B g\left(\vec{\hat{S}}_1 + \vec{\hat{S}}_2\right) \cdot \vec{B}$$

$$S_1 \xrightarrow[\quad]{J_1} S_2$$

$$S_1 = S_2 = \frac{1}{2}$$

The importance of a model

» Do some toy calculations to understand the what the parameters in your model do!



The importance of a model

» WARNING!

» g is very poorly determined by susceptibility measurements!

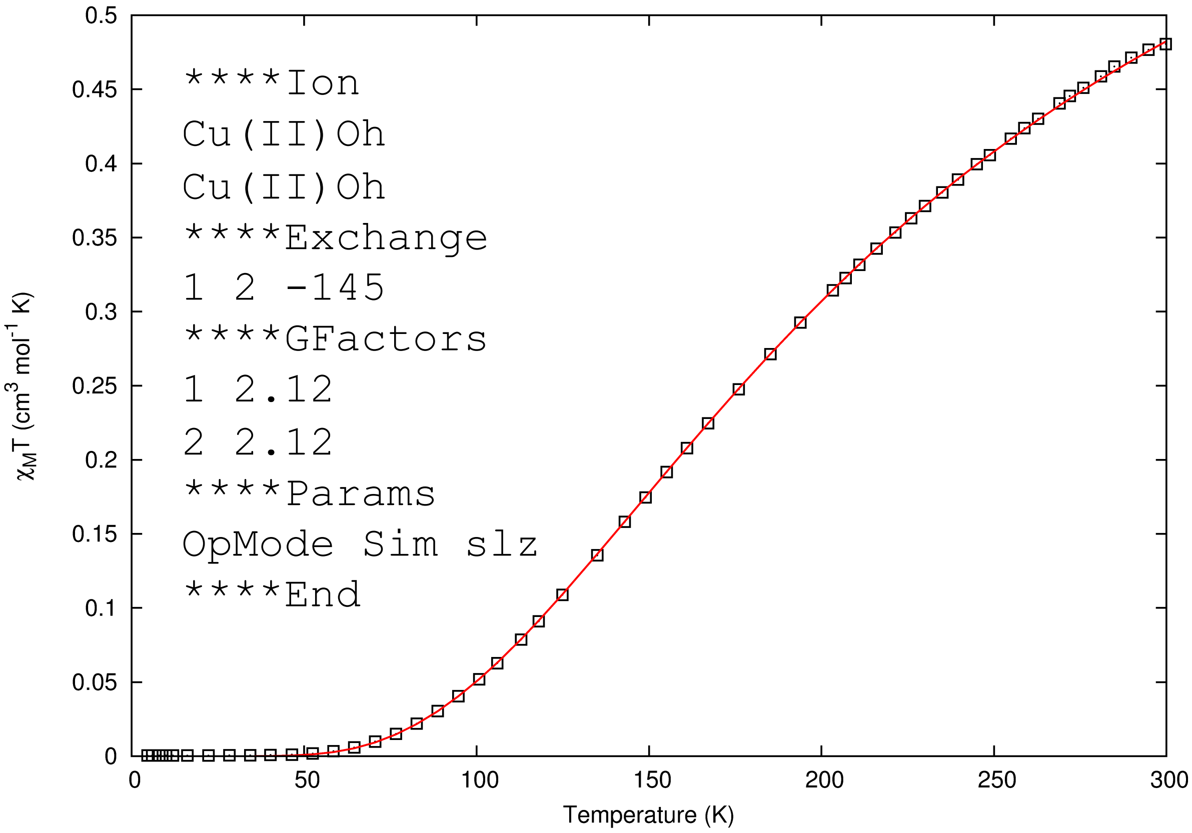
» This is due to approximate diamagnetic corrections and sample masses as well as purity

» Must use EPR to determine these accurately!

The importance of a model

» Do some simulations or fits to determine the best parameters for your model

» May not be unique!



The importance of a model

$$J_1 = -145\ cm^{-1}$$
$$g = 2.12$$

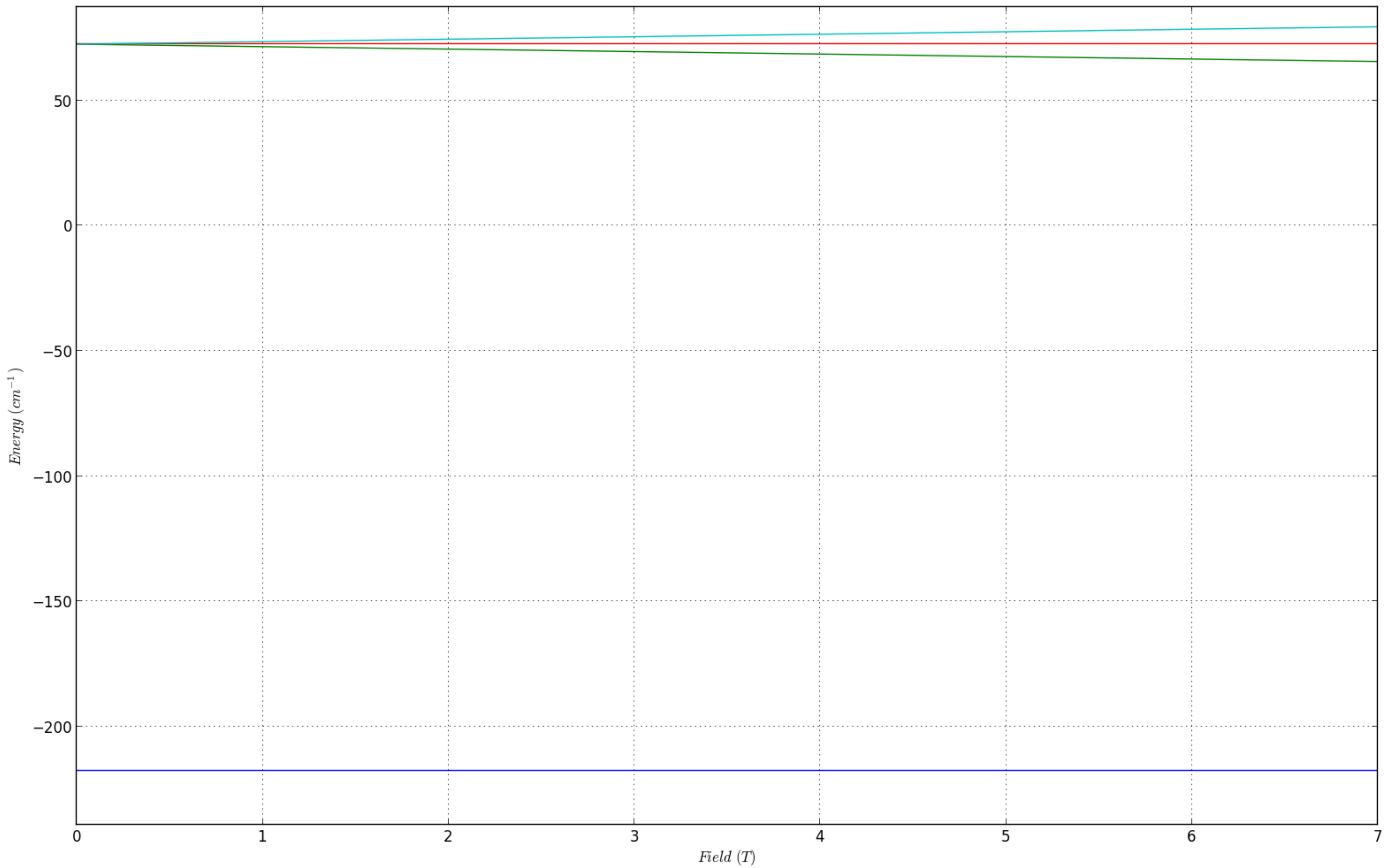
» Look at what the eigenstates are!

```
---------------------------------------
Eigenstates (Wavefunction coefficients)
---------------------------------------


E cm-1         0.0000E+00  0.2900E+03  0.2900E+03  0.2900E+03

  mS(1) mS(2)
  -0.5  -0.5               1.00000000
  -0.5   0.5  0.70710678                           0.70710678
   0.5  -0.5 -0.70710678                           0.70710678
   0.5   0.5                           1.00000000

------------------------------------
Eigenstates (Percentage Composition)
------------------------------------


E cm-1         0.0000E+00  0.2900E+03  0.2900E+03  0.2900E+03

  mS(1) mS(2)
  -0.5  -0.5              100.0000000
  -0.5   0.5  50.0000000                           50.0000000
   0.5  -0.5  50.0000000                           50.0000000
   0.5   0.5                          100.0000000
```

The importance of a model

» Look at what the eigenstates are!

$$J_1 = -145\ cm^{-1}$$
$$g = 2.12$$



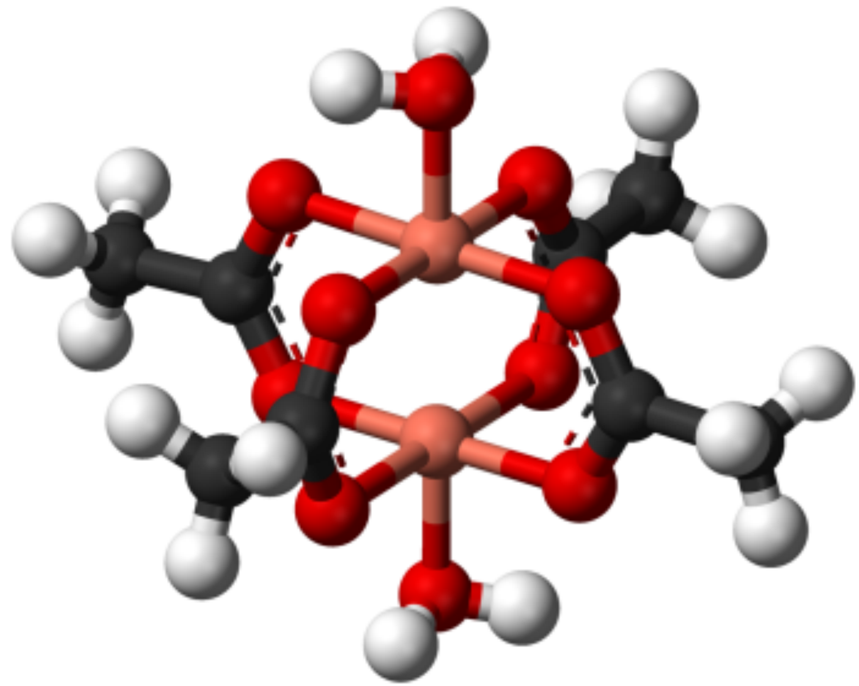
The importance of a model

» Finally come back to the sketch and the molecule and interpret what your measurements are telling you!

$$S_1 \overset{J_1}{\text{———}} S_2$$

$$J_1 = -145\ cm^{-1}$$

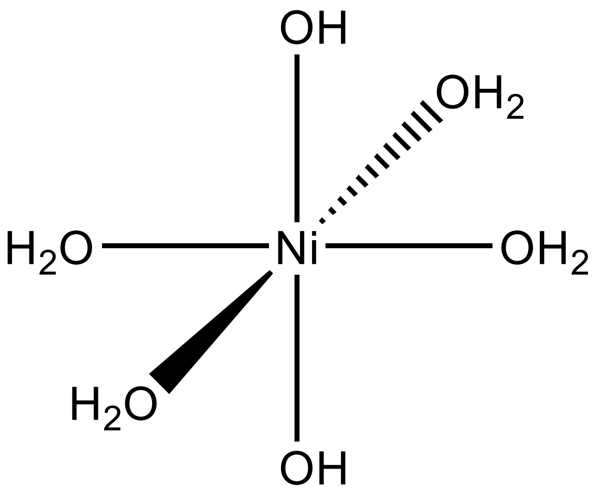
$\uparrow$ $\downarrow$

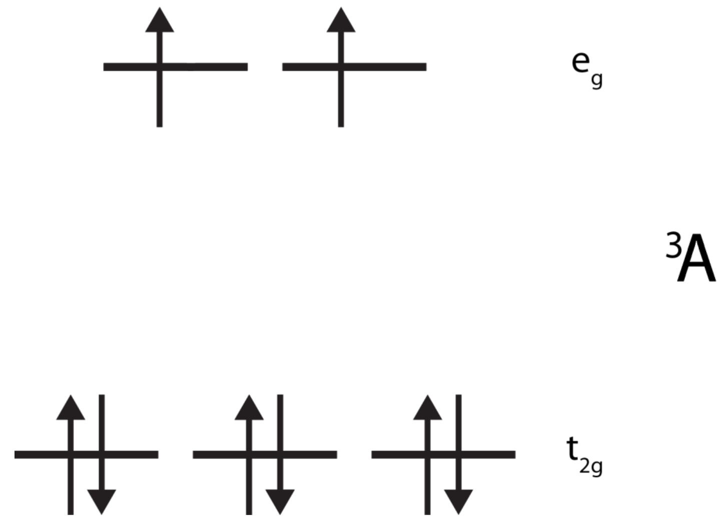


The importance of a model

Ni^{II} example

» Our sketch.....of an imaginary complex...



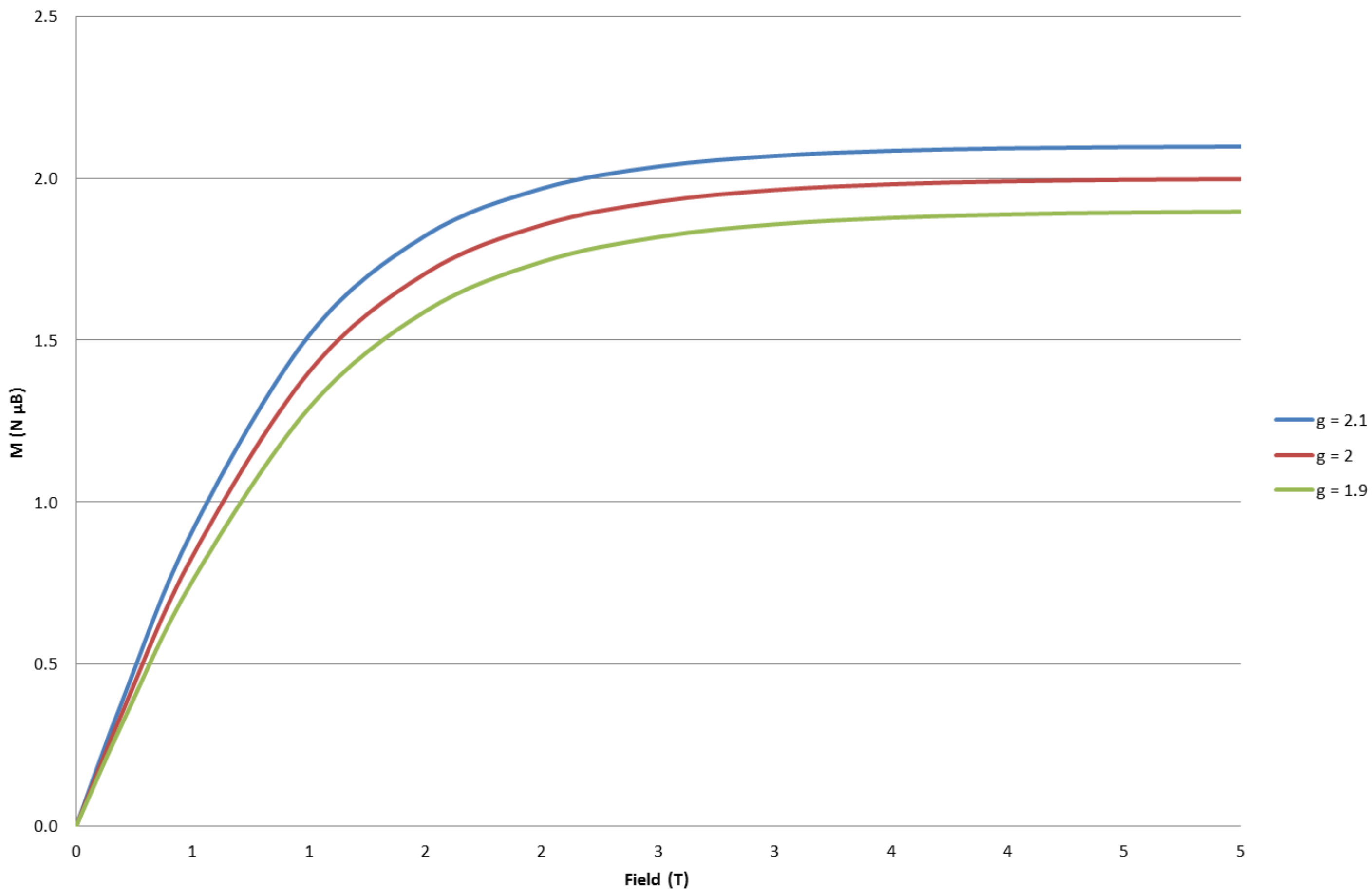


$$S = 1$$

$$\hat{H} = D\left(\hat{S}_z^2 - \frac{1}{3}S(S+1)\right) + \mu_B g \hat{S} \cdot \vec{B}$$

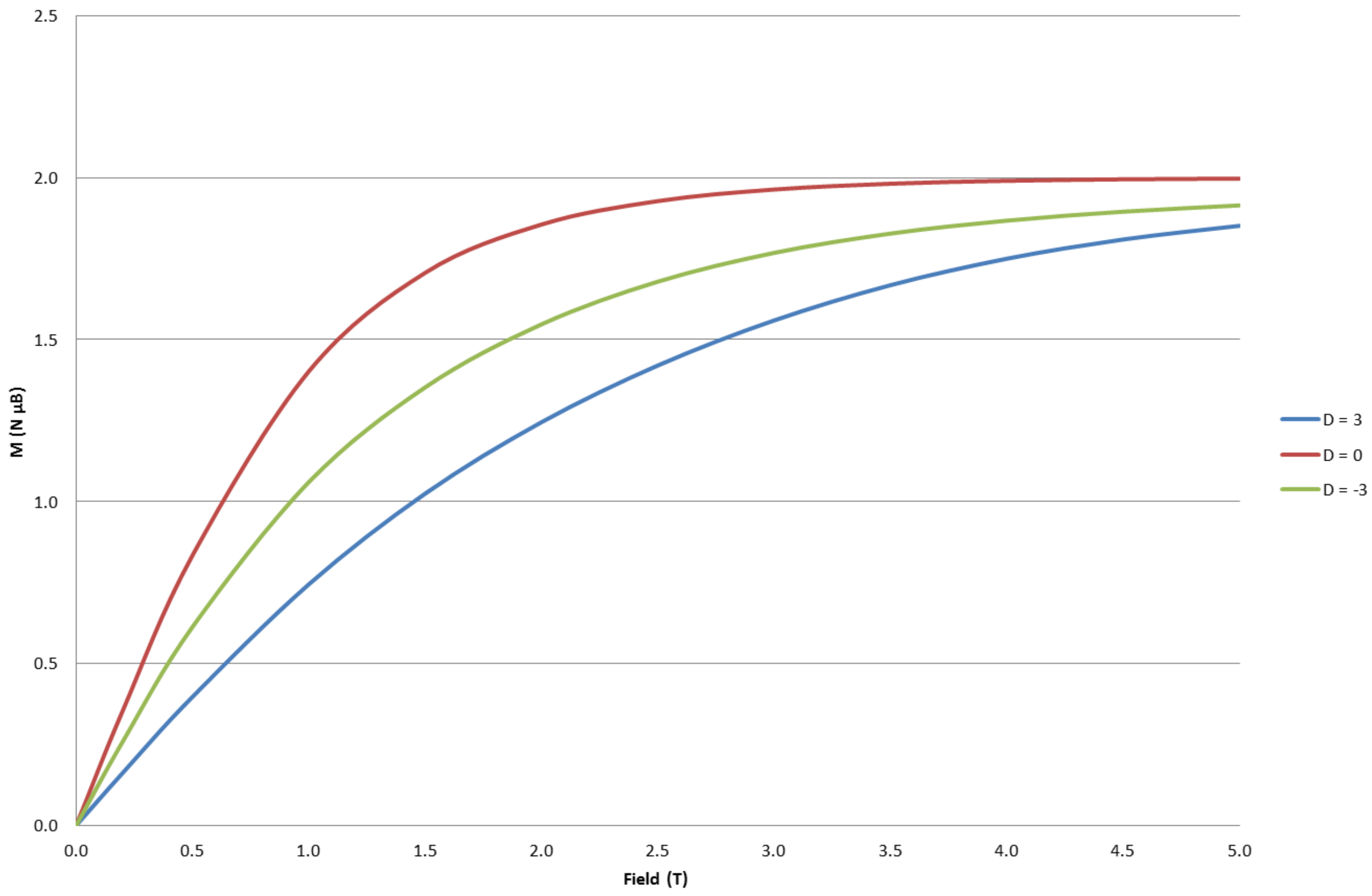
Ni^{II} example

» Effect of g on magnetization



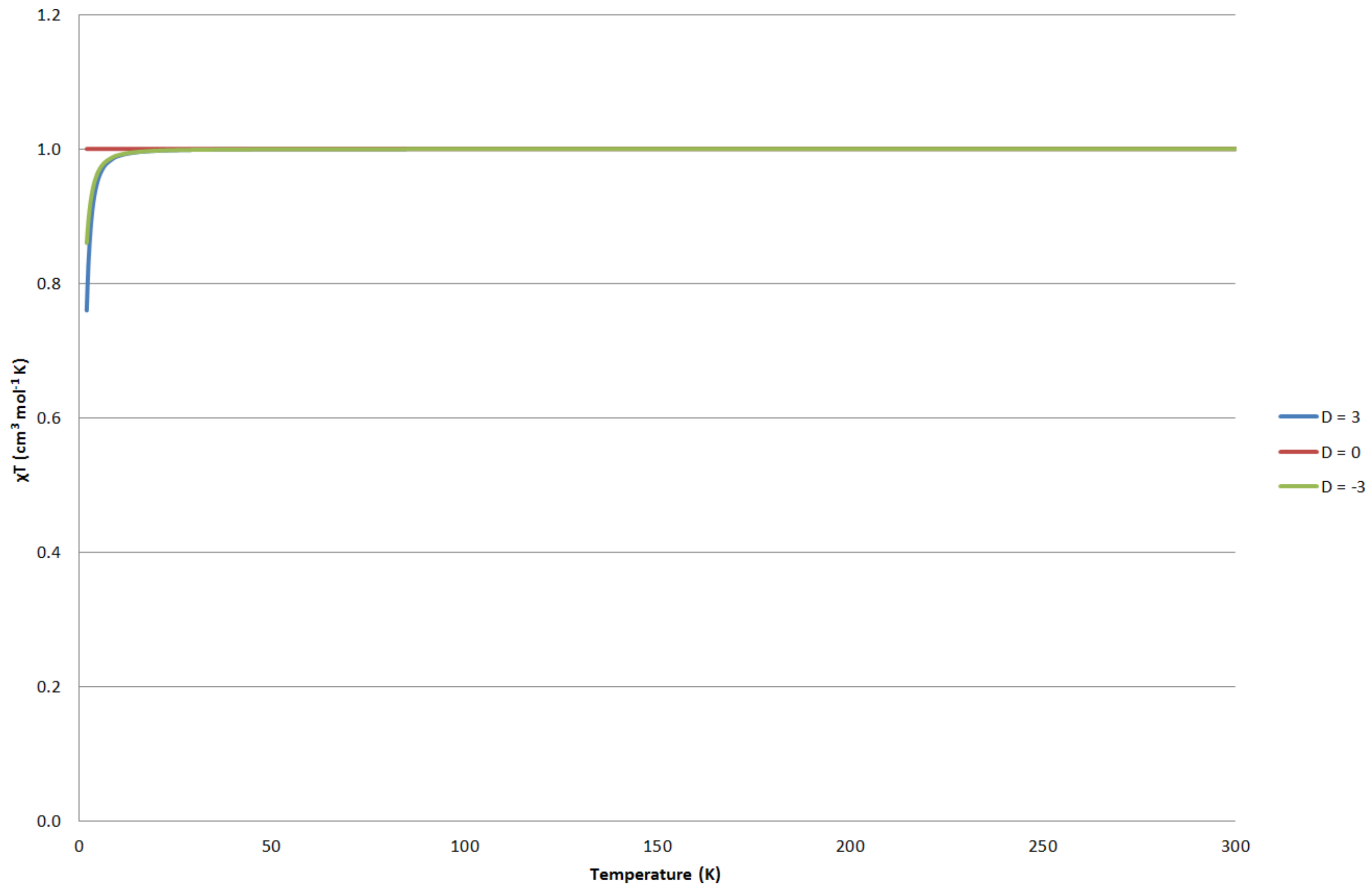
Ni^{II} example

» Effect of D on magnetization



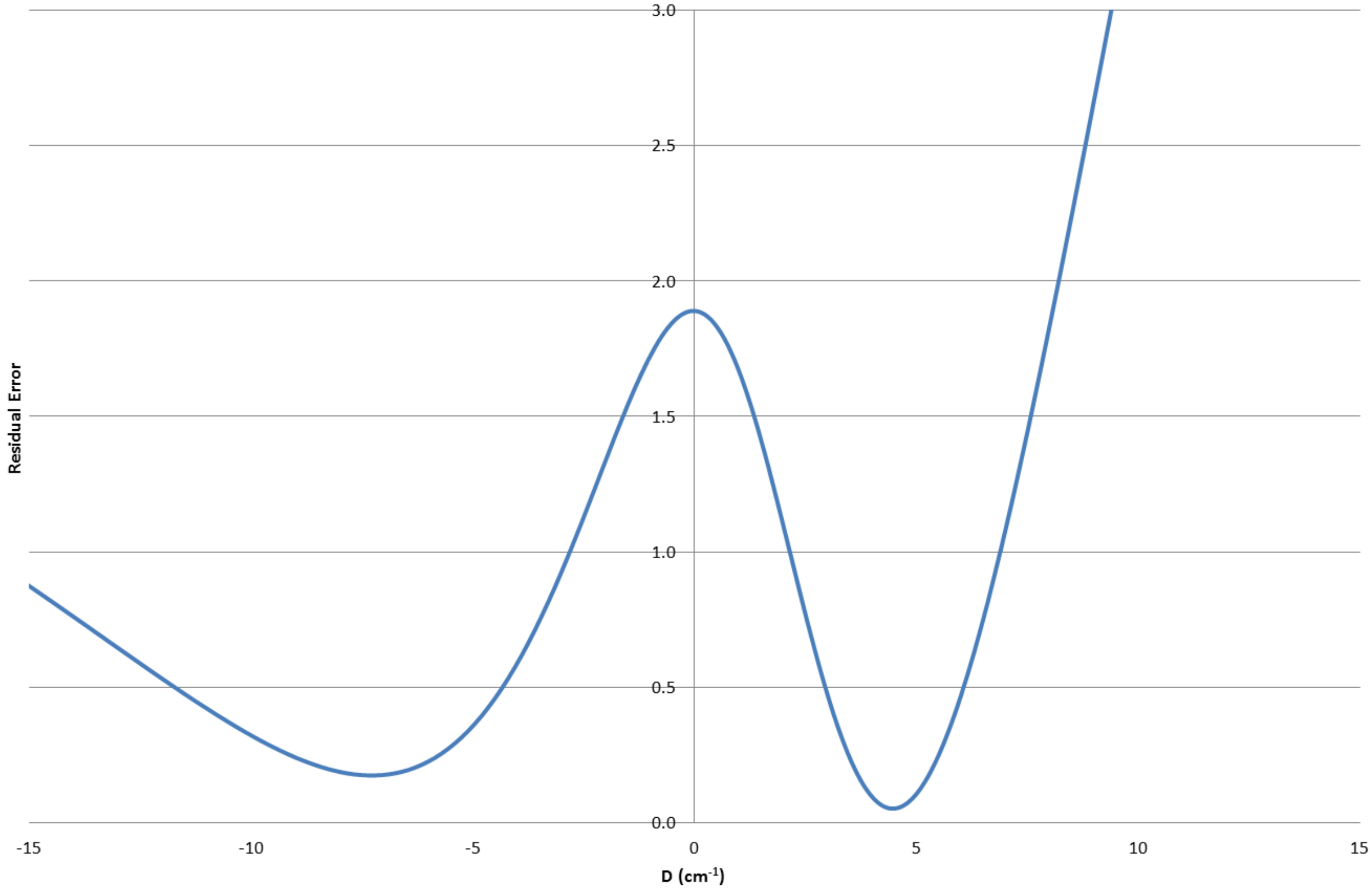
Ni^{II} example

» Effect of D on susceptibility



Ni^{II} example

» WARNING! The sign of D is very poorly determined by magnetization measurements!



Ni^{II} example

Single ion vs. cluster D

» Consider the spin system:

$$S_1 \overset{J_1}{\text{―――――}} S_2$$

$$S_1 = S_2 = 1$$

» When coupled, we get S = 0, S = 1 and S = 2

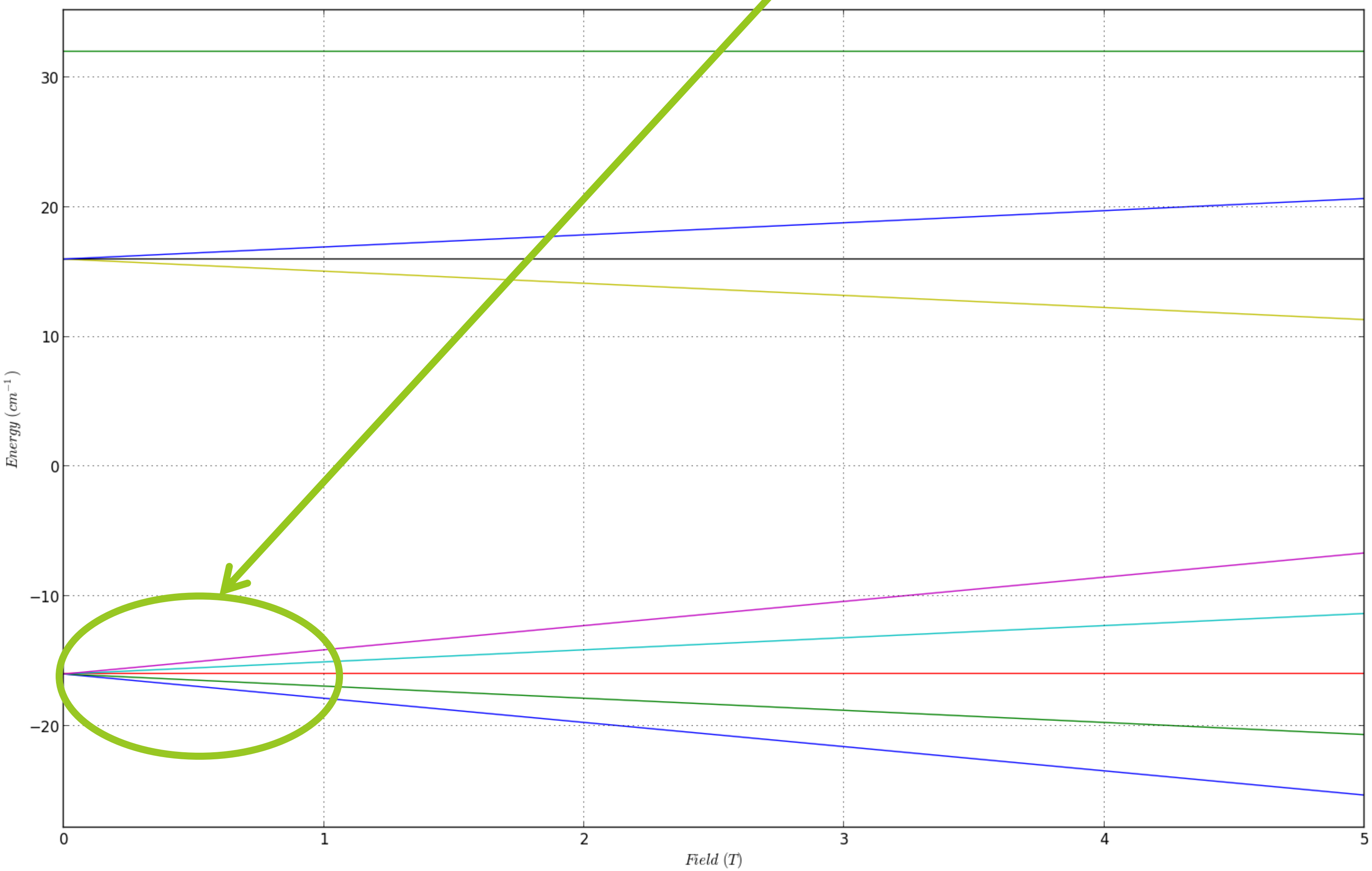
» S = 2 is the ground state if the coupling is ferromagnetic

$$\hat{H} = -2J\vec{\hat{S}}_1 \cdot \vec{\hat{S}}_2 + \mu_B\left(g_1\vec{\hat{S}}_1 + g_2\vec{\hat{S}}_2\right) \cdot \vec{B}$$

Single ion vs. cluster D

» The Zeeman spectrum:

Low fields and temperatures, looks like S = 2



Single ion vs. cluster D

» Two ways we could model the behaviour:

$$\hat{H} = -2J\vec{\hat{S}}_1 \cdot \vec{\hat{S}}_2 + \mu_B\left(g_1\vec{\hat{S}}_1 + g_2\vec{\hat{S}}_2\right) \cdot \vec{B}$$
$$+d_1\left({\hat{S}_{1_z}}^2 - \frac{1}{3}S_1(S_1+1)\right) + d_2\left({\hat{S}_{2_z}}^2 - \frac{1}{3}S_2(S_2+1)\right)$$

$$\hat{H} = D\left(\hat{S}_z^2 - \frac{1}{3}S(S+1)\right)$$

Single ion vs. cluster D

Reasonable parameter ranges

» Unless you know better, g ≈ 2

» For 3d ions, g can vary due to close lying orbitally degenerate excited states

» For $d^1 - d^4$, g < 2

» For $d^6 - d^9$, g > 2

» Don't go below 1.9 or above 2.3, unless you have spectroscopic proof!

Reasonable parameter ranges

- For 3d metals, |J| < 50 cm^{-1} (usually, Cu^{II} exception)
- For 4f metals, |J| < 2 cm^{-1}

- For 3d metals, |D| < 10 cm^{-1} (usually)
- For isotropic Gd^{III}, D is negligible (observable in EPR)
- For other Ln^{III}, CF is a very important perturbation

Reasonable parameter ranges

Error residuals and Unique fits

» So what is this 'R-value' or 'residual'?

» In PHI (for example);

$$R = \sum_i \left(\chi_{exp}{}^{i} - \chi_{calc}{}^{i}\right)^2 \times \sum_j \left(M_{exp}{}^{j} - M_{calc}{}^{j}\right)^2$$

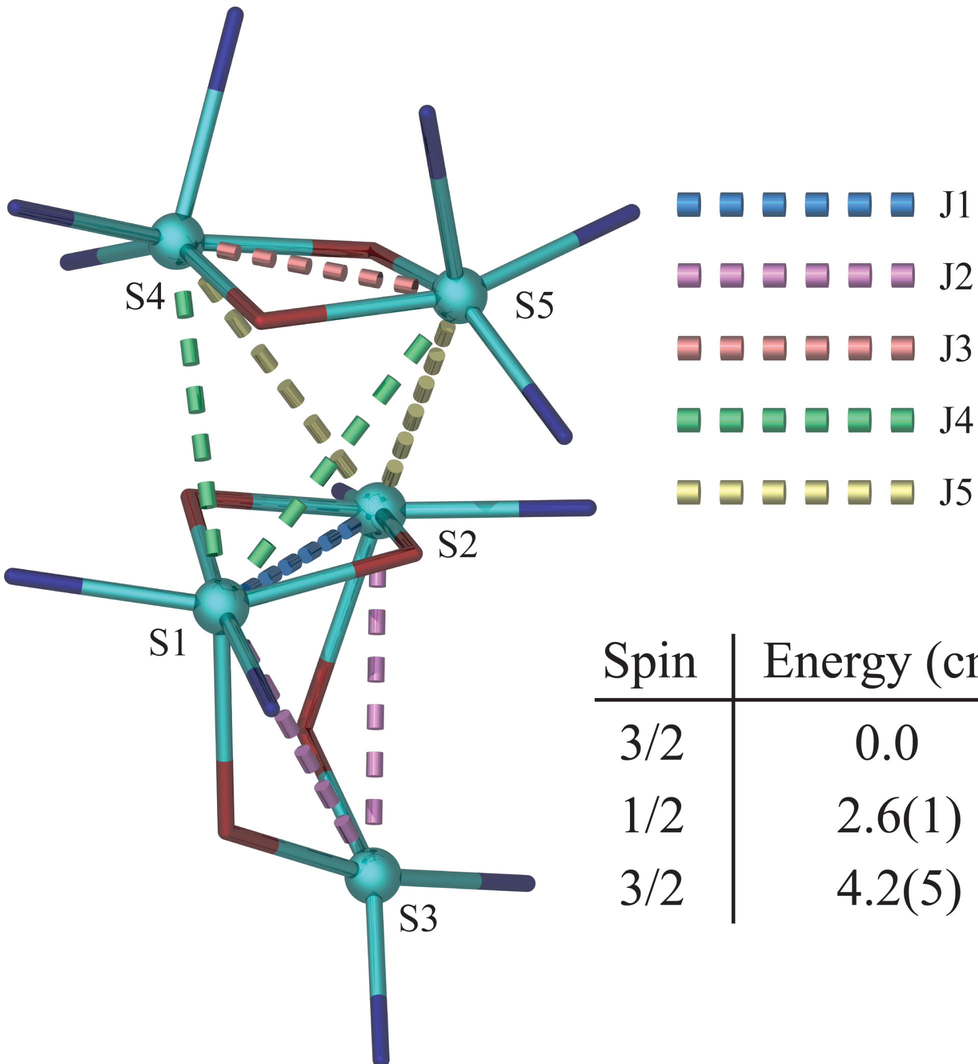
» Only meaningful within one dataset!!

- » i.e. for your experimental data
- » Fitting χ and M together will have different R values than fitting them separately!

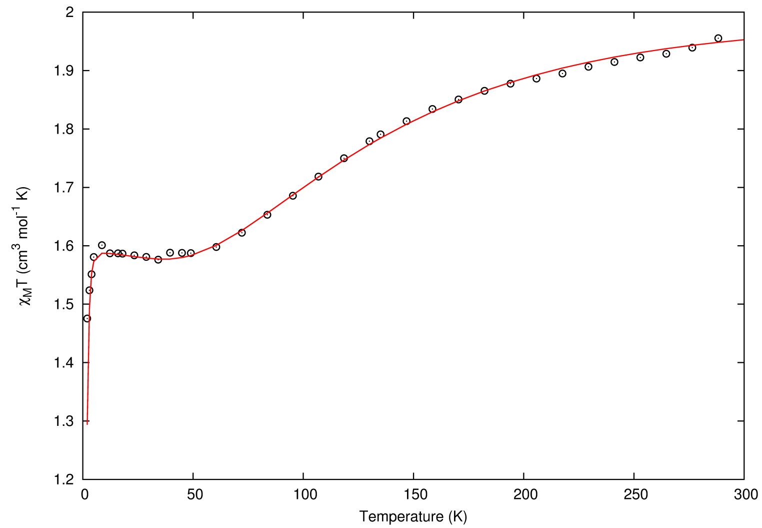
» Consider experimental uncertainty – don't just believe the numbers! Use your eyes to distinguish good from bad fits!

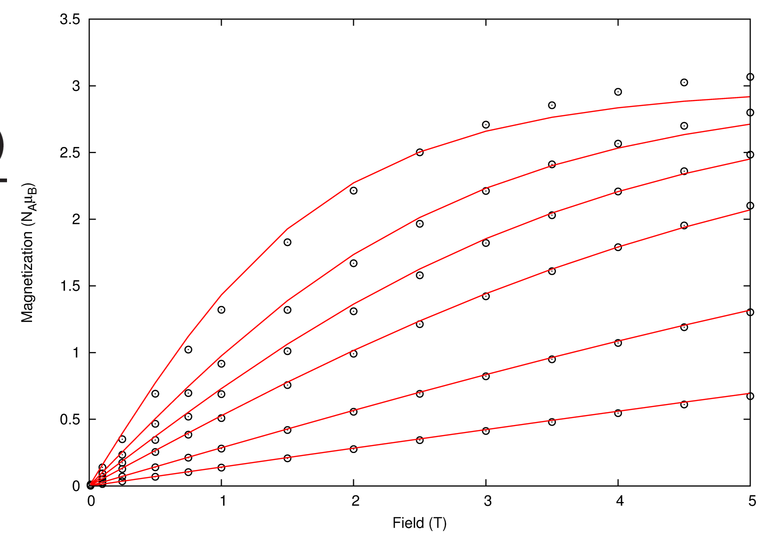
Error residuals and unique fits

» Not always one parameter set!



Spin	Energy (cm^{-1})
3/2	0.0
1/2	2.6(1)
3/2	4.2(5)





Error residuals and unique fits

- To-do list:
  - More efficient matrix diagonalization (Sparse, Davidson, Lanczos, etc.)
  - Point group symmetry simplifications
  - New and efficient EPR approach
  - EPR roadmaps
  - Frequency-swept EPR
  - New minimization algorithms
  - True self-consistent mean-field intermolecular interaction

… any other ideas?

New features in PHI