

On the origin of Magnetic Anisotropy and how it creeps into Molecular Nanomagnets

Outline

I. Electron Spin and where it comes from in Physics

II. Effective Hamiltonians

Notation

space: mathematical space such as vector space, Hilbert space

space: our daily's life 3-dimensional space \Rightarrow will be called henceforth orbital space

operators are indicated by a hat

I. Electron Spin and where it comes from in Physics

I.1. Schrödinger Equation

kinetic energy + electrostatic potential

\rightarrow wavefunction in orbital space three coordinates

$$\Psi \equiv \Psi(x, y, z) = \Psi(\vec{r})$$

I.2. Pauli Equation

electron spin is introduced phenomenologically

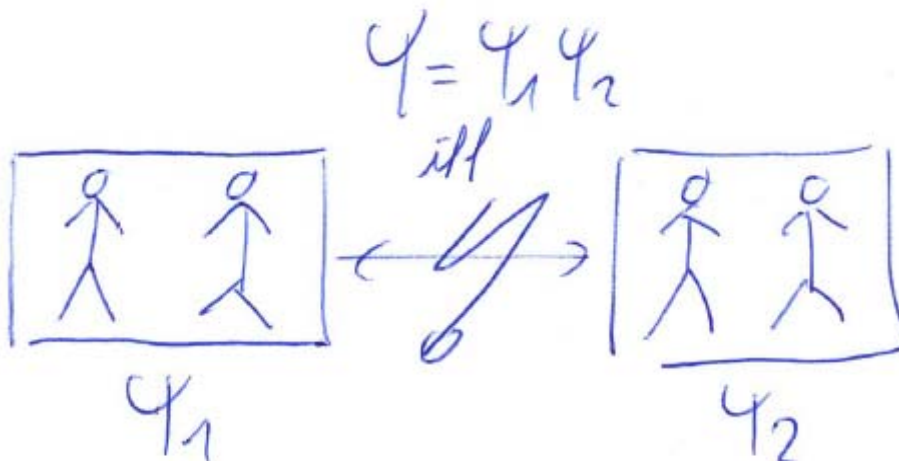
\rightarrow the space is extended to orbital and spin space

$$\Psi \equiv \Psi(x, y, z)\sigma(m_s)$$

\rightarrow interactions with magnetic fields, $\hat{\mu} = -g\mu_B \hat{s}$, with $s = 1/2$

\rightarrow g undetermined by theory, plugged in from experiment

Note: the spin degree of freedom is like a forth coordinate! it's kind of independent
no interaction between two "areas/spaces" \Leftrightarrow wavefunction separable into product states



I.3. Dirac Equation

relativistic extension of the Schrödinger Equation

→ describes fermions with spin $s = 1/2 \Rightarrow$ orbital and spin spaces predicted

→ existence of antiparticles

→ interaction with magnetic fields, $\hat{\mu} = -g\mu_B \hat{s}$, with $s = 1/2$ and $g = 2.0000$

→ spin-orbit interaction $\hat{H}_{so} = -\frac{e^2}{2m^2 c^2} \hat{s}(\vec{E} \times \hat{p})$

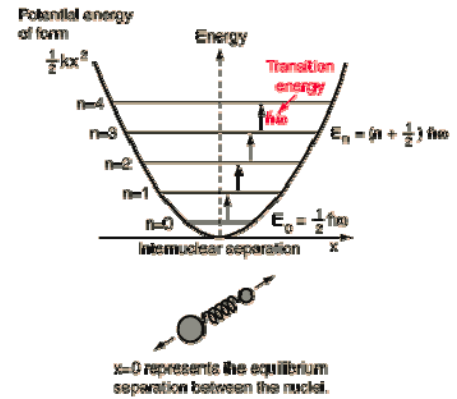
I.4. Quantum Electrodynamics (QED)

the vacuum is not empty and silent, there are always quantum fluctuations because of Heisenberg uncertainty principle

Example:

harmonic oscillator = zero point motions, $E_n = \hbar\omega \left(n + \frac{1}{2} \right)$

in contrast to a classical harmonic oscillator, which will be at rest at zero energy, a quantum mechanical harmonic oscillator can't be at rest even in the lowest eigen state or ground state, since the uncertainty principle forbids $\Delta x = 0$, it hence must oscillate, as is also seen by the fact that the minimal energy is not zero



this very same happens with electric and magnetic fields

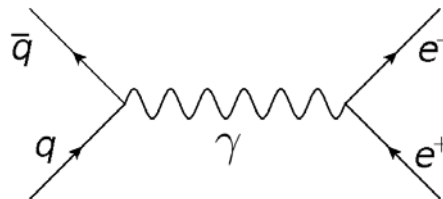
\Rightarrow vacuum quantum fluctuations

→ particle-antiparticle generation out of vacuum

→ virtual particles (you can borrow the energy for a short time to generate a particle)

→ eich bosons transmit interactions/forces between charges

in QED the eich boson related to the Coulomb force are the photons



\Rightarrow any force is related to a certain particle and vice versa any force requires the existence of a particle (see also e.g. Higgs research)

the good thing is, the vacuum quantum fluctuations are observable:

→ Lamb shift of $2s_{1/2}$ and $2p_{1/2}$ levels in Hydrogen atom (lift of degeneracy in j)

→ Casimir force

→ $g = 2.00231930436153$

I.5. The Standard Model

This is our current model of "everything".

How is the Schrödinger equation related to the standard model?

Standard Model

*limit model to photons
i.e. charges i.e. Coulomb force*

Dirac equation

*consider only particles
(no antiparticles) and their behavior
at "low" energies*

Pauli equation + magnetic field + spin-orbit interaction

the latter equation is the equation that we (i.e. Liviu and friends) use in "daily" live, it derives from the fundamental Standard Model as approximation to our situation of interest

Note: The latter equation (i.e. Coulomb forces + spin + magnetic field + spin orbit-interaction) is commonly called just Schrödinger Equation. We henceforth will do so too.

I.6. The free Electron and first conclusions

What have we learned so far, e.g. for the properties of a free electron is

→ orbital and spin contributions to wave function

→ $s = 1/2$

→ interaction with magnetic fields $\hat{\mu} = -g\mu_B \hat{s}$ with $g = 2.0023$

→ spin-orbit interaction

Conclusions most relevant to us:

⇒ interaction with magnetic fields allow us to see and manipulate what the spin is doing in its space

⇒ spin-orbit interaction lets the spin feel what the electrostatic fields (and their symmetries) are in orbital space (our "real" space)

Question: What is the origin of magnetic anisotropy?

Valid answers:

Answer 1: quantum mechanics (because without the concept of spin would not be possible)

Answer 2: special relativity (because without spin would not exist)

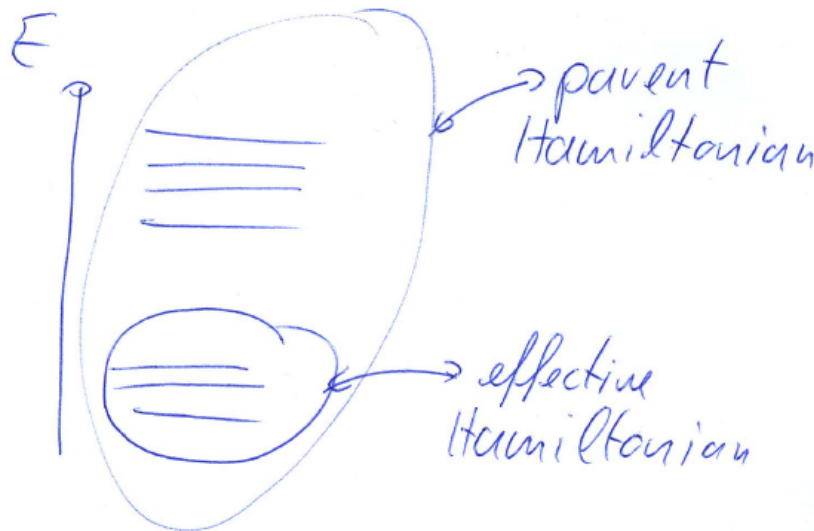
Answer 3: spin-orbit interactions because:

orbital space can be anisotropic because of e.g. ligands, and the spin can feel this anisotropy only through spin-orbit interactions

II. Effective Hamiltonians

II.1. What the heck is that?

We have seen now how the spin and our Schrödinger Equation emerges from the "fundamental" Standard Model, namely by looking just at a small part of the full energy spectrum and/or the low-energy part of the spectrum



In other words: we (can) derive a model we use for daily work from a more fundamental model by just looking at the low energies

→ this produces another Hamiltonian, which narrows down the scope and can't describe "everything" anymore, but is (usually) easier to handle.

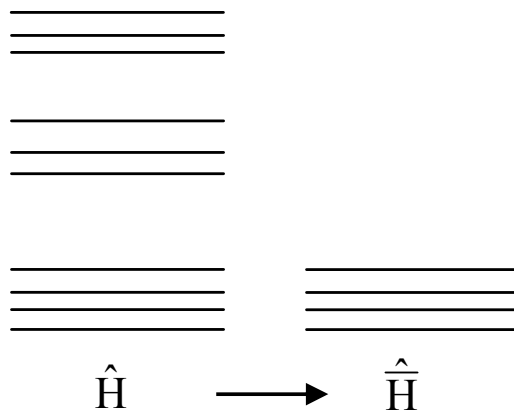
This Hamiltonian is also called an **effective Hamiltonian**.

Example: With our Schrödinger equation we can't describe nuclear fission, the big bang, etc. pp,

II.2. What the heck is that really?

Formally we ALWAYS can do the following:

Goal: Ensure that the energies for both the parent H and the effective H are identical for the selected states!



Spectrum of original (parent) H

Spectrum of effective H

Note: One doesn't have to pick the N lowest eigen states, in principle one could pick out any N states of the spectrum... but I don't know any case there we would do that!

The effective Hamiltonian can, in principle, be found very easily: One just has to place the selected "real" energy values of the parent Hamiltonian on the diagonals of a matrix:

$$\hat{H}^{eff} = \begin{pmatrix} \ddots & & & \\ & E_2 & & \\ & & E_1 & \\ & & & E_0 \end{pmatrix} \Leftrightarrow E_n = \langle n | \hat{H} | n \rangle = \langle n | \hat{H}^{eff} | n \rangle = E_n^{eff}$$

Example 1: The simplest effective Hamiltonian

----- $\Rightarrow \hat{H}^{eff} = E_{gs} \hat{1} = E_{gs} (1)$

Test: $\hat{H}\Psi = E_n \Psi \Rightarrow n = 0$ and $E_0 = E_{gs}$

Example 2: Effective Hamiltonian for two and more states

we wish to pick 2 states from our original Hamiltonian, usually the two lowest states, e.g. a Kramers doublet

==== $\Rightarrow \hat{H}^{eff} = \begin{pmatrix} E_1 & 0 \\ 0 & E_0 \end{pmatrix}$, 2-dim matrix \Rightarrow two eigenstates

Eigenbasis	Any Basis
$\hat{H}^{eff} = \begin{pmatrix} E_1 & 0 \\ 0 & E_0 \end{pmatrix}$	$\hat{H}^{eff} = V^{-1} \begin{pmatrix} E_1 & 0 \\ 0 & E_0 \end{pmatrix} V = \begin{pmatrix} a & c + id \\ c - id & b \end{pmatrix}$

Decomposition using a trivial set of basis matrices

$$\hat{H}^{eff} = a \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + (c + id) \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + (c - id) \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + b \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Decomposition using angular momentum matrices

$$\hat{H}^{eff} = \frac{1}{2}(a + b) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2}(a - b) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + c \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - d \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Reformulation in terms of angular momentum operators

$$\hat{H}^{eff} = \frac{1}{2}(a + b)\hat{1} + (a - b)\hat{s}_z + 2c\hat{s}_x - 2d\hat{s}_y$$

Example 3: we can trivially extend this to any (finite) number of selected states
Quickly sketch the scheme for 3 states

Question: What is one trying to do with an effective Hamiltonian?

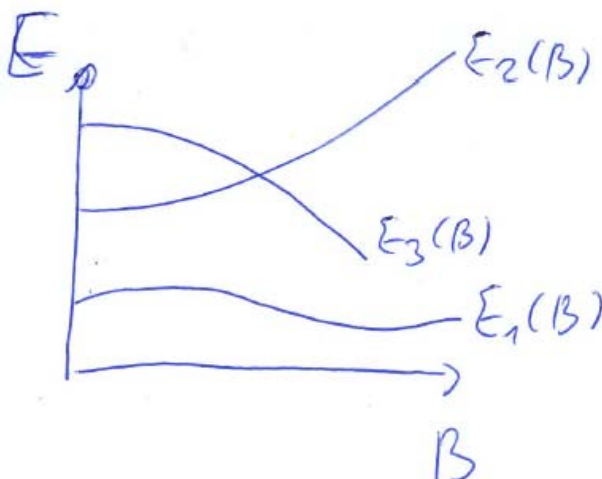
Answer: One wants to describe the ENERGIES of a limited number of eigenstates of the real system correctly

Question: What should we do if we don't know the real energy values at the first place?

Answer: Do experiments, find a proper effective Hamiltonian and determine the parameters phenomenologically, and then leave the rest to the theoreticians

II.3. How does the magnetic field enter?

So far we just had eigen states those energies were "constant", however in reality they can change with an externally applied "field", e.g. magnetic fields (or pressure)(NOT temperature!!!!)

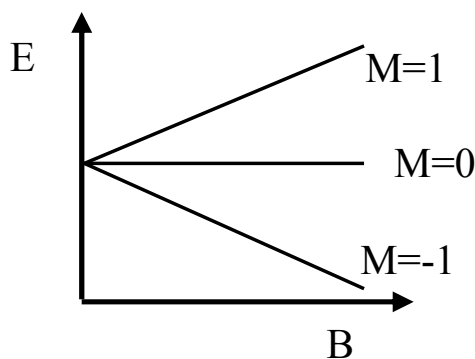


$$\Rightarrow E_n \equiv E_n(B)$$

$$\Rightarrow \hat{H}^{eff} \equiv \hat{H}^{eff}(B)$$

\Rightarrow the parameters which add the basis matrices or operator basis become field dependent!

Example 1: The second simplest effective Hamiltonian?



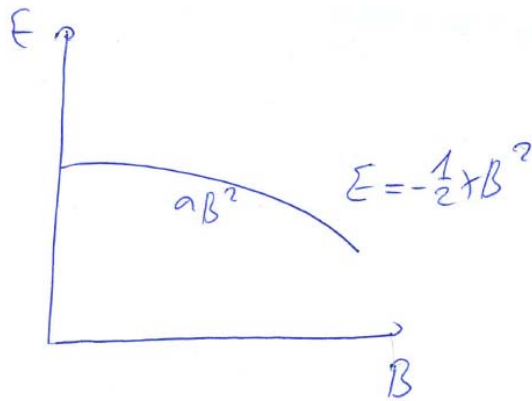
$$\Rightarrow \hat{H}^{eff} = g\mu_b B \hat{s}_z$$

\Rightarrow paramagnetism, Brillouin function

Comment:

- This usually emerges from a 1st-order perturbation theory of the paramagnet Hamiltonian (1st-order because B^1)

Example 2: Temperature independent paramagnetism and/or diamagnetism



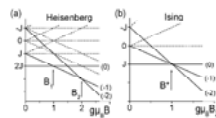
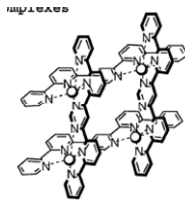
$$\Rightarrow \hat{H}^{eff} = -\frac{1}{2} \chi B^2$$

$$\Rightarrow E = -\frac{1}{2} \chi B^2 \Leftrightarrow m = -\frac{\partial E}{\partial B} = \chi B$$

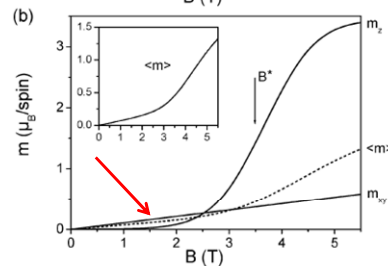
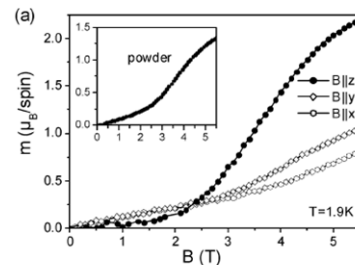
Comments:

- This usually emerges from a 2nd-order perturbation theory of the parent Hamiltonian (2nd-order because B^2)
- You ALWAYS will have such a term in your effective Hamiltonian, it is only usually not considered (and sometimes with good reasons)(but not always!)
- This can compromise seriously efforts to determine an effective g-matrix from measurements of the anisotropic magnetic susceptibility tensor at low fields. A striking example is the case of meta-magnetic behavior in the Co[2x2] grid, Inorg. Chem. 45, 6535 (2006).

Metamagnetic Behaviour in a Co[2x2] Grid



$$\hat{H}_{2 \times 2} = -J \sum_{i=1}^3 (\hat{S}_{i,z} \hat{S}_{i+1,z} + \hat{S}_{4,z} \hat{S}_{1,z}) + \mu_B \sum_{i=1}^4 g_i \hat{S}_{i,z} B_z - \frac{1}{2} \chi_0 (B_x^2 + B_y^2)$$



OW *et al*, Inorg. Chem. 45, 6535 (2006)

II.4. How does the ligand field enter

Ligand fields lead to a splitting of the energy spectrum even without any applied magnetic field. Depending on the situation this is called ligand field splitting, Stark levels, zero-field splitting, but fundamentally its all the same.

$\Rightarrow \hat{H}^{eff} \equiv \hat{H}^{eff} (B = 0)$, \Rightarrow Stevens operators provide a basis of matrices to describe that

II.5. How do magnetic interactions enter?

For polynuclear clusters magnetic interactions lead to a additional spitting of the energy spectrum in zero field, which is not accounted for by the ligand field splittings.

$$\Rightarrow \text{exchange terms, } \Rightarrow -\hat{S}_i \vec{J}_{ij} \hat{S}_j, \left(\hat{S}_i \hat{S}_j \right) \left(\hat{S}_k \hat{S}_l \right)$$

(projection operators provide a basis of matrices to describe that)

II.6. What's up with the wavefunction?

Our goal was to have the ENERGIES of the parent and effective Hamiltonian to coincide, i.e.

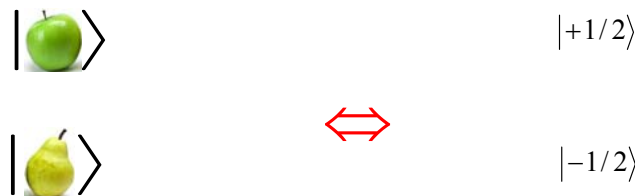
$$E_n = \langle n | \hat{H} | n \rangle = \langle n | \hat{H}^{eff} | n \rangle = E_n^{eff}$$

But: since only the expectation values should coincide we do NOT have to use the same wavefunctions on both sides of this equation!

$$\Rightarrow \langle n | \hat{H} | n \rangle = \langle n |^{eff} \hat{H}^{eff} | n \rangle^{eff}$$

Example 1: Spin, Apples and Pears

A Space of Apple and Pears



$$\hat{H}_{fruits} = \begin{pmatrix} a & c+id \\ c-id & b \end{pmatrix} \qquad \hat{H}_{spin} = \begin{pmatrix} a & c+id \\ c-id & b \end{pmatrix}$$

Hamiltonians for the spin system and the fruit system:

Apple-Pear space: $|n\rangle^{eff} = \left| \begin{array}{c} \text{apple} \\ \text{pear} \end{array} \right\rangle, \hat{H}_{fruits} = \begin{pmatrix} a & c+id \\ c-id & b \end{pmatrix}$

$s = 1/2$ Spin Space: $|n\rangle = | +1/2 \rangle, | -1/2 \rangle, \hat{H}_{spin} = \begin{pmatrix} a & c+id \\ c-id & b \end{pmatrix}$

$$\hat{H}_{spin} = \hat{H}_{fruit}$$

$$|n\rangle \neq |n\rangle^{eff}$$

- ⇒ (1) \hat{H}_{spin} can be used as effective Hamiltonian for describing the fruits
- ⇒ (2) \hat{H}_{fruit} can be used as effective Hamiltonian for describing the spins

Example 2: Heisenberg Hamiltonian

Exchange Splitting in Hydrogen

Schrödinger equation with Coulomb forces
 +
 Pauli anti-symmetrization principle
 =
 pure electrostatic Hamiltonian

$$E_+ = \int \varphi_a \left(\frac{p^2}{2m} + \frac{1}{r} \right) \varphi_a$$

$$E_- = \int \varphi_s \left(\frac{p^2}{2m} + \frac{1}{r} \right) \varphi_s$$

$$\hat{H}_{orbitalspace} = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix} \Leftrightarrow \hat{H}_{totalspinspace} = \begin{pmatrix} E_{S=1} & 0 \\ 0 & E_{S=0} \end{pmatrix}$$

⇒ Heisenberg exchange is NOT a "real" spin interaction
 it can be though described effectively as a spin interaction

Consequence:

We can map one problem onto another one (iff they have the same energy spectrum). This is an EXTREMELY powerful technique in physics.

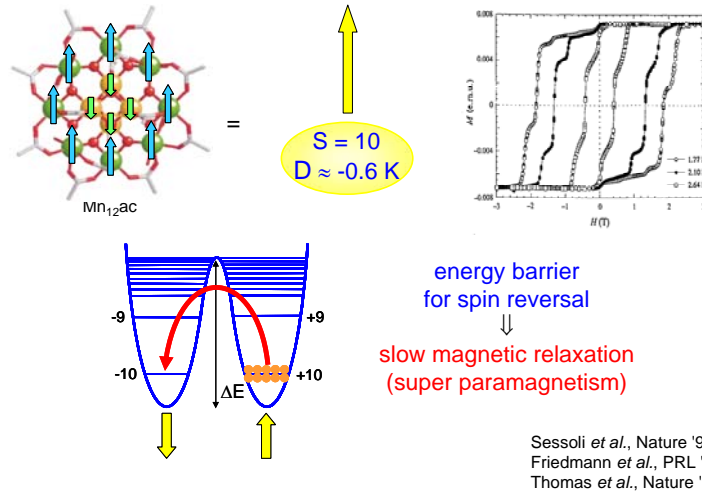
Question: What is a physicist?

Answer: A physicist is a person who is happy only if she/he can describe a real world phenomena with an as strange as possible model

Examples:

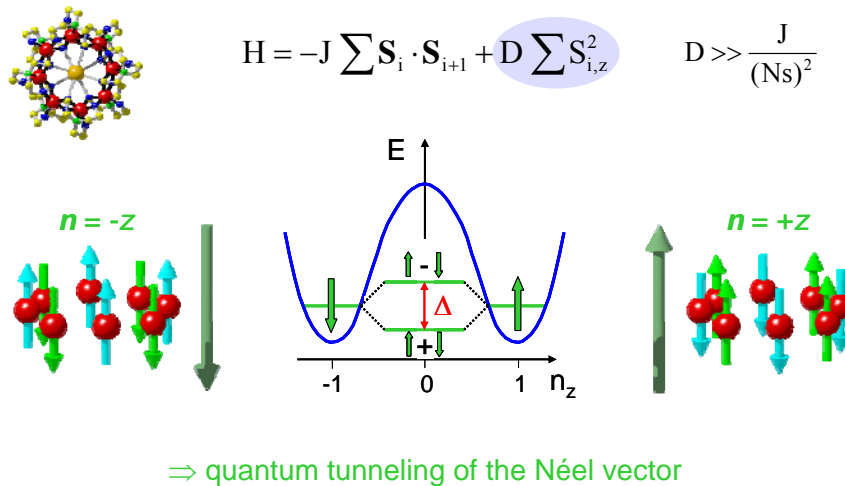
- Spin ice
- Quantum tunneling of the magnetization: A phenomena familiar in orbital space can also be realized and observed in this "strange" spin space

Slow Magnetic Relaxation in Mn₁₂ac



- Quantum tunneling of the Neel vector: A phenomena familiar in orbital space can also be realized and observed in an even more "strange" space...

Heisenberg Rings with Easy-Axis Anisotropy



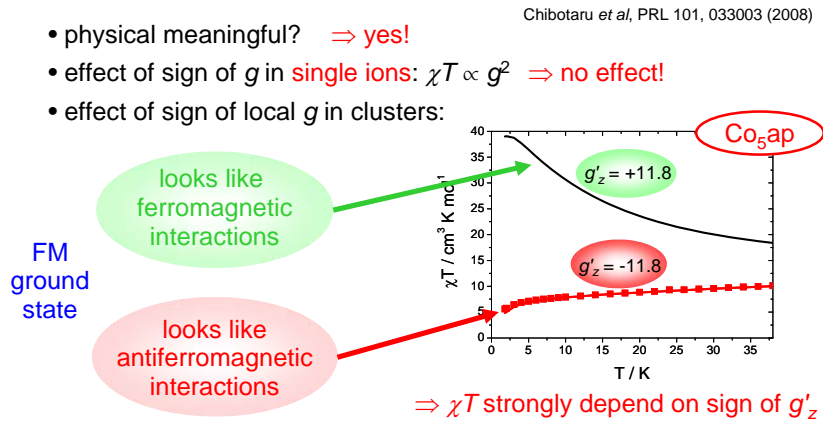
Comments:

- Often the wave functions of the effective Hamiltonian derive from the parent wave functions in perturbation theory and it holds $|n\rangle^{eff} \approx |n\rangle$
- The effective Hamiltonian obviously allows to directly calculate/simulate THERMODYNAMIC quantities such as magnetization, susceptibility, specific heat, as here on the energies enter.
- However, in order to calculate spectroscopic quantities, such as EPR or INS, correctly one in addition has to modify the operators in the matrix elements, since the wave functions have changed (this is - for no reason - generally neglected!!!)
- It can be hard to figure out the significance of the parameters in the effective Hamiltonian, i.e. their relation to "reality"

Examples:

- The coefficients in the g matrix can be for instance negative. This can dramatically change the behavior of e.g. the χT curve.

The Sign of the $g_{\alpha\beta}$ Factors

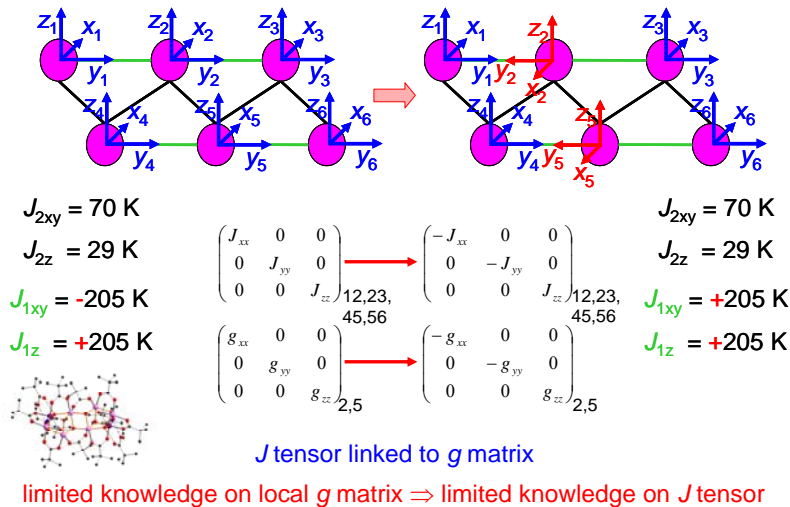


ferromagnetic interactions + negative g factors
 $\Rightarrow \chi T$ can look antiferromagnetic

F. Klöwer, Y.-H. Lan, J. Nehrkor, OW, C. E. Anson, AKP, Chem. Eur. J. 15, 7413 (2009)

- There can be a large number of "different" Hamiltonians which are in fact identical.

Local Coordination Frames in $\text{Co}^{\text{II}}_6\text{Co}^{\text{III}}_2$



II.8. What is this all good for?

For the analysis one may wish to use **more than one** effective model, depending on the range of energies relevant for a certain discussion

Typical: low-lying Kramers doublets, low-lying exchange-split energies, ligand field levels

Hence it is important to

- understand the concept
- understand that we can switch between models
- understand the limitation and range of validity of each model
- keep carefully track of the level of sophistication involved (significance of parameters)