Basic Magnetism

1. Paramagnetism and Diamagnetism (macroscopic)

external magnetic field $\vec{H}$

diamagnetic   paramagnetic
sample   sample
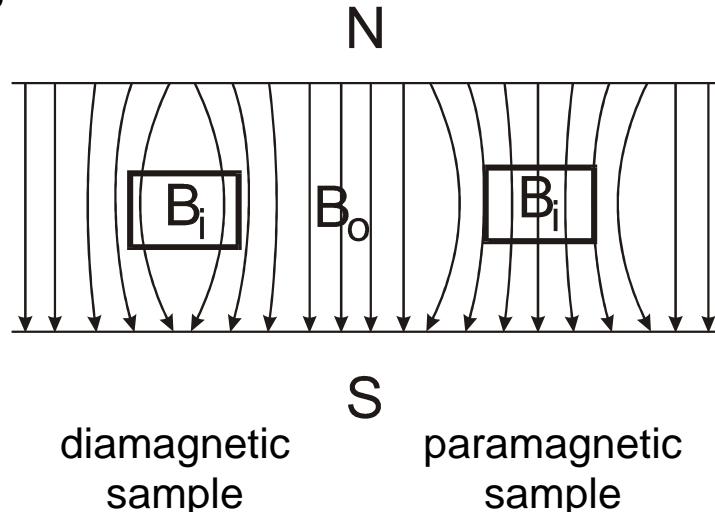
$\vec{B}$: magnetic induction (magnetic field intensity inside sample)

$$\vec{B} = \vec{H} + 4\pi\vec{M}$$

$\vec{M}$: intensity of magnetization (magnetic moment $\vec{\mu}$ / unit volume)

$B_i < B_o$ $B_i > B_o$

$B_i = \mu_r \bullet B_o$ μ_r: relative magnetic permeability

$\mu_r < 1$ $\mu_r > 1$

$B_i = B_o + B'$
$B' = \chi_v \bullet B_o$ χ_v: volume susceptibility (unit less)

$\chi_v < 0$ $\chi_v > 0$

measurement: Faraday balance, SQUID, ...

χ_m^{mes}: molar susceptibility

$\chi_m^{mes} = \chi_m^{para} + \chi_m^{dia}$ χ_m^{dia} from tables, Pascal's constants

$$\chi_m^{para} = \chi_m^{mes} - \chi_m^{dia}$$

2. Paramagnetism
2.1. Microscopic interpretation

♦ must relate macroscopic susceptibility to the magnetic dipole moments $\vec{\mu}$ of N_A molecules

classical

no $\vec{H}$ $\vec{H}$

∞ orientations
∞ states of same
energy $E^{(0)}$

$E = -\vec{\mu}\,\vec{H}$

② — $+\mu\,H$

Boltzman
distribution

① — $-\mu\,H$

E

$E^{(0)}$
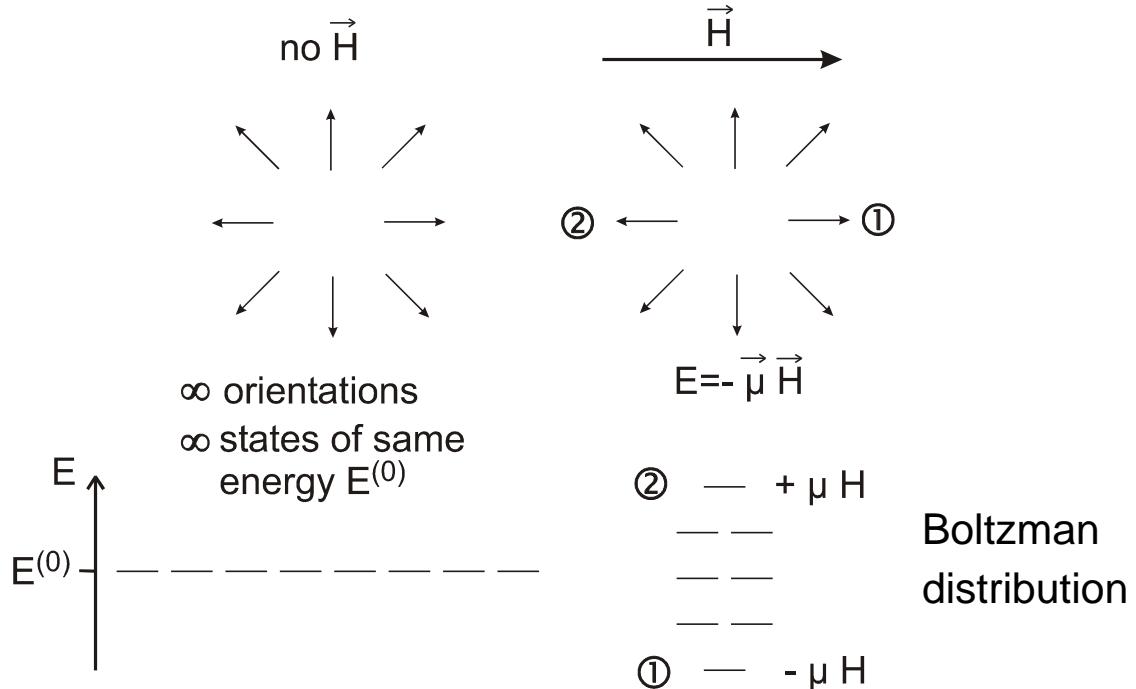
♦ total energy of system lowered by external magnetic field

$$\boxed{M = -\frac{\partial E}{\partial \mathrm{H}}}$$

→ sample attracted into field

quantum mechanics

♦ molecule with energy levels E_n ($n = 1, 2, ...$) in the presence of magnetic field $\vec{H}$ → microscopic magnetization μ_n

$$\mu_n = -\frac{\partial E_n}{\partial H}$$

macroscopic molar magnetization M_m by partition function:

(no approximation)

$$\boxed{M_m = N_A \frac{\sum\limits_n \left(-\frac{\partial E_n}{\partial H}\right) \cdot \exp\left(-\frac{E_n}{kT}\right)}{\sum\limits_n \exp\left(-\frac{E_n}{kT}\right)}}$$

$$\chi_m = \frac{\partial M_m}{\partial H}$$

in a weak field: χ_m is independent of H

$$\chi_m = \frac{M_m}{H}$$

2.2. The van Vleck equation

approximation: $E_n = E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2$ $(+...)$

$$\mu_n = -\frac{\partial E_n}{\partial H} = -E_n^{(1)} - 2E_n^{(2)}H \quad (-...)$$

$$M_m = N_A \frac{\sum\limits_n \left(-E_n^{(1)} - 2E_n^{(2)}H\right) \cdot \exp\left(-\frac{E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2}{kT}\right)}{\sum\limits_n \exp\left(-\frac{E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2}{kT}\right)}$$

further approximations:

♦ $\boxed{\dfrac{H}{kT} \langle\langle\, 1}$

♦ $\exp(x) \approx 1 + x$ for $x \langle\langle\, 1$

♦ for $H \to 0 \;\;\Rightarrow\;\; M \to 0$ $\qquad \sum_n \left(-E_n^{(1)} \right) \cdot \exp\left(-\dfrac{E_n^{(0)}}{kT} \right) = 0$

♦ $E_n^{(2)} H^2 \approx 0$

♦ $E_n^{(2)} E_n^{(1)} \approx 0$

$$M_m = H \cdot N_A \cdot \frac{\displaystyle\sum_n \left[\left(\dfrac{E_n^{(1)^2}}{kT} - 2E_n^{(2)} \right) \cdot \exp\left(-\dfrac{E_n^{(0)}}{kT} \right) \right]}{\displaystyle\sum_n \exp\left(-\dfrac{E_n^{(0)}}{kT} \right)}$$

$$\boxed{\chi_m = N_A \cdot \frac{\displaystyle\sum_n \left[\left(\dfrac{E_n^{(1)^2}}{kT} - 2E_n^{(2)} \right) \cdot \exp\left(-\dfrac{E_n^{(0)}}{kT} \right) \right]}{\displaystyle\sum_n \exp\left(-\dfrac{E_n^{(0)}}{kT} \right)}}$$

- need energies of the system under investigation
- plug into equation (Van Vleck or - better - the partition function)
- calculate χ_m
- compare to experiment and gain insight into the electronic structure of the system under investigation

2.3. *S* = ½ **system, Zeeman effect, Curie law**

free electron spin S = ½ m_s = +1/2, m_s = -1/2,
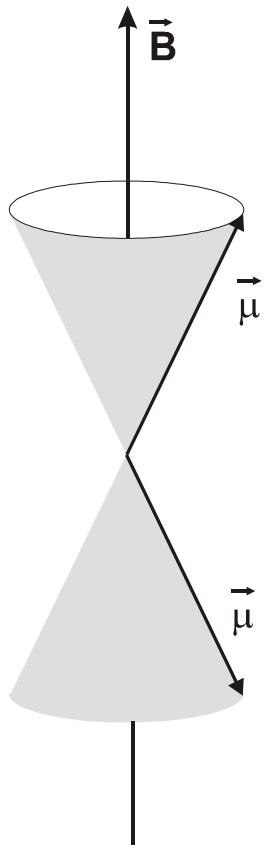
m_S = - 1/2

E = - 1/2 μ_B g B

determined: $\left|\vec{\mathbf{S}}^2\right|$ und S_z

undetermined: S_x und S_y

m_S = 1/2

E = 1/2 μ_B g B

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

$$\hat{S}_z \left| S, m_S \right\rangle = m_S \left| S, m_S \right\rangle$$

$$\hat{S}^2 \left| S, m_S \right\rangle = S(S+1) \left| S, m_S \right\rangle$$

$$\mu_B g B \hat{S}_z \left| \frac{1}{2}, \frac{1}{2} \right\rangle = \mu_B g B * \frac{1}{2} \left| \frac{1}{2}, \frac{1}{2} \right\rangle \qquad \left| \frac{1}{2}, \frac{1}{2} \right\rangle \qquad \frac{1}{2} \mu_B g B$$

$$\mu_B g B \hat{S}_z \left| \frac{1}{2}, -\frac{1}{2} \right\rangle = \mu_B g B * \left(-\frac{1}{2} \right) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \qquad \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \qquad -\frac{1}{2} \mu_B g B$$

$$E = -\overline{\boldsymbol{\mu}} \cdot \vec{\mathbf{B}}$$

E $m_S = +1/2$

$\mu = -\tfrac{1}{2} g\, \mu_B$

$\mu = -\mu_B$

$E^{(0)}$

$m_S = -1/2$

$\mu = \tfrac{1}{2} g\, \mu_B$

$\mu = \mu_B$

$\vec{H}$
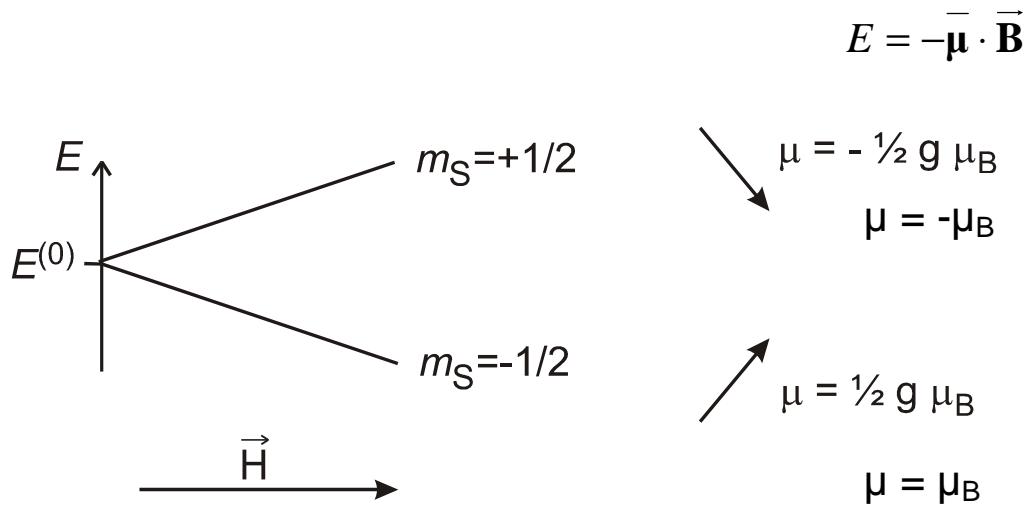
♦ $E_n = M_S \mu_B g B$ plug into Van Vleck equation

$$\chi_m = N_A \cdot \frac{\displaystyle\sum_n \left[\left(\frac{E_n^{(1)^2}}{kT} - 2E_n^{(2)} \right) \cdot \exp\left(-\frac{E_n^{(0)}}{kT} \right) \right]}{\displaystyle\sum_n \exp\left(-\frac{E_n^{(0)}}{kT} \right)}$$

$$E_n = E_n^{(0)} + E_n^{(1)}B + E_n^{(2)}B^2 \qquad ; \quad E_n^{(0)} = 0, \quad E_n^{(1)} = M_S \mu_B g, \quad E_n^{(2)} = 0$$

$$\chi = \frac{N_A}{kT} \cdot \frac{\displaystyle\sum_{M_s=-S}^{+S}(M_S \mu_B g)^2}{2S+1} \quad \text{using} \quad \sum_{i=-n}^{n} i^2 = \tfrac{1}{3}(2n+1)(n+1)n$$

$$\boxed{\chi = \frac{N_A}{3kT} \cdot \mu_B^{\,2} g^2 S(S+1) = \frac{C}{T} \quad \text{mit} \quad C = \frac{N_A}{3k} \cdot \mu_B^{\,2} g^2 S(S+1)}$$

Curie law

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♦ effective magnetic moment, μ_{eff}:

$$\frac{\mu_{eff}}{\mu_B} = \sqrt{\frac{3k}{N_A \cdot \mu_B{}^2}} \cdot \sqrt{\chi \cdot T} = 2.827915 \cdot \sqrt{\chi \cdot T} = g_e \sqrt{S(S+1)}$$

spin-only !!!

♦ graphical representation calculated for $S = ½$ and $g = 2.00$
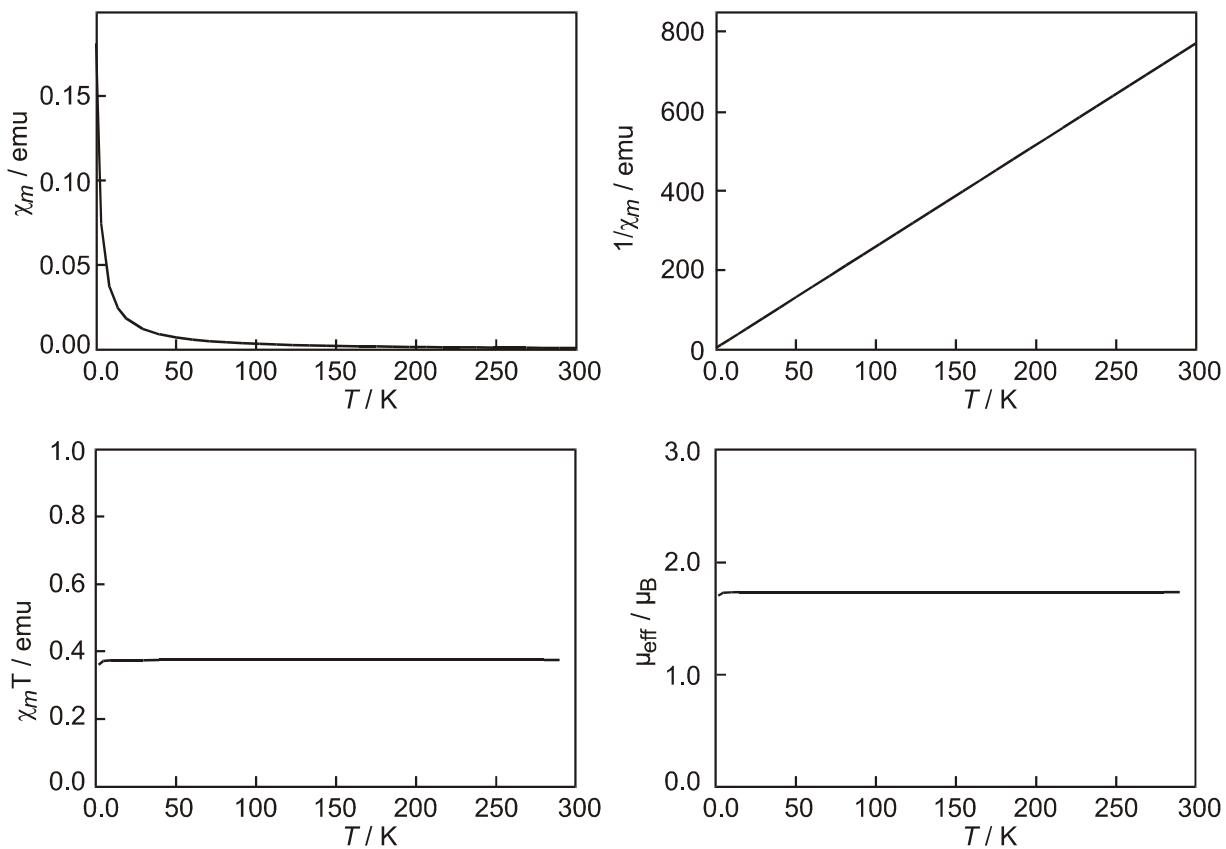
S	χT / cm^3 K mol^{-1}	μ_{eff} / μ_B
1/2	0.375	1.73
1	1.000	2.83
3/2	1.876	3.87
2	3.001	4.90
5/2	4.377	5.92

2.4. Saturation effects and Brillouin function

♦ general isotropic system with spin state S

$E = M_S \mu_B g B$ plug into the partition function for M_m

$$M_m = -N_A g\mu_B \frac{\sum\limits_{M_s} M_s \cdot \exp\left(-\dfrac{g\mu_B B M_s}{kT}\right)}{\sum\limits_{M_s} \exp\left(-\dfrac{g\mu_B B M_s}{kT}\right)}$$

....

$$M_m = N_A g\mu_B S \cdot B_S(x) \qquad \text{with} \qquad x = \frac{g\mu_B B}{kT}$$

with $$B_S(x) = \frac{\left(S+\frac{1}{2}\right)\coth\left[x\left(S+\frac{1}{2}\right)\right] - \frac{1}{2}\coth\left(\frac{x}{2}\right)}{S}$$
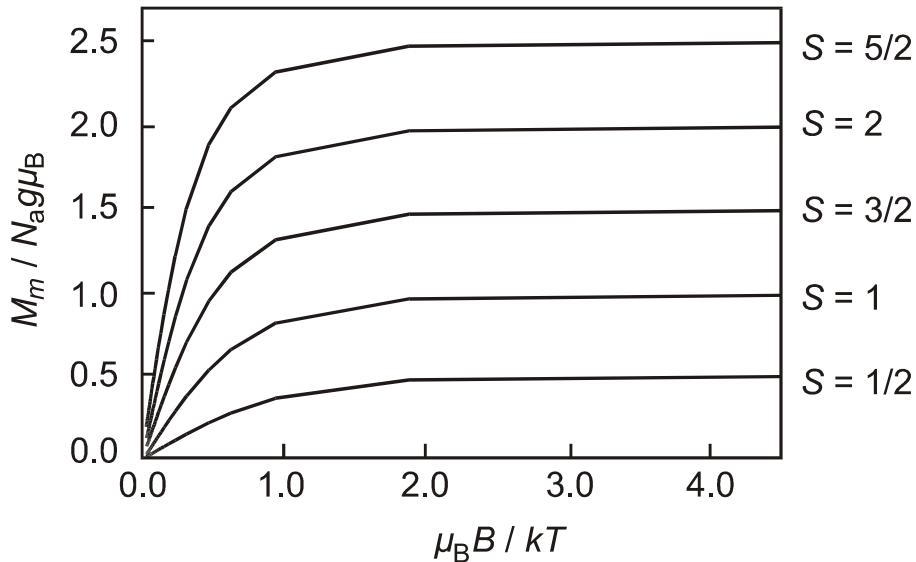
♦ low x values: linear - Curie behavior
   Note: Curie law: $M_m \propto B$

♦ high x values: saturation - only $M_s = -S$ populated

2.5. Zero-field splitting: SO coupling in system < cubic symmetry
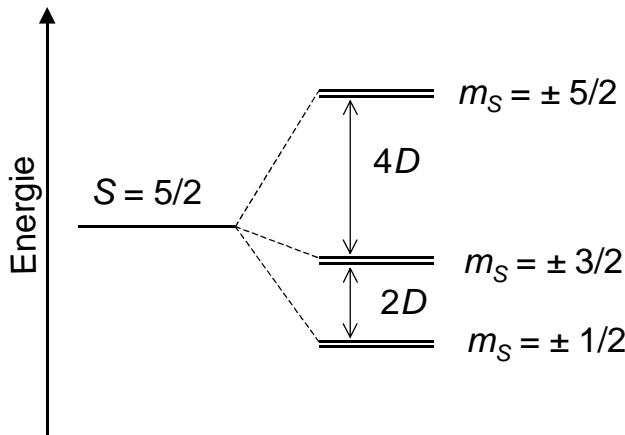
♦ zero-field spin Hamiltonian

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

♦ combined effect of so coupling and symmetry lowering:
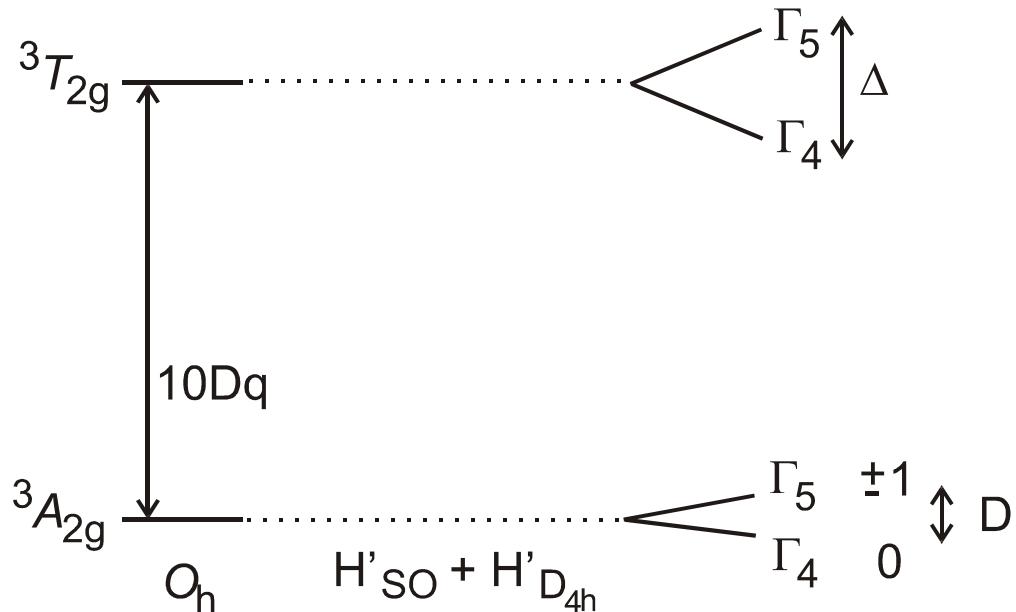
from second order perturbation theory in λLS in D_{4h}: $D = \dfrac{8\lambda^2 \Delta}{(10Dq)^2}$

2.6. Temperature Independent Paramagnetism   TIP

2. Order Zeeman effect

$$\chi_m{}^{mes} = \chi_m{}^{para} + \chi_m{}^{dia} \qquad (\chi_m{}^{para}: \text{positive}; \chi_m{}^{dia}: \text{negative})$$

$$\boxed{\chi_m{}^{para} = C \,/\, T + \chi_{TIP}}$$

$$\chi_{TIP} \quad \text{positive !!! and small}$$

◆ Example: Cu^{II} in octahedral symmetry

$$\chi_{TIP} = \frac{4k^2 N\mu_B^2}{10Dq} = \frac{4 \cdot 0.64 \cdot 0.261}{10000} = 67 \cdot 10^{-6} \text{cm}^3\text{mol}^{-1}$$

with $N\mu_B^2 = 0.261$,   10 Dq in cm^{-1} and χ in cm^{3}mol^{-1} (cgs emu)

compare to $\chi_m{}^{para}$ ~ 1500 cm^{3}mol^{-1} at 300 K

◆ famous example: Co^{III} l.s. (d^6) χ_{TIP} ~ 600 cm^{3}mol^{-1} ($S = 0$)

◆ Note: χ_{TIP} is temperature independent in χ !!!!

effects on μ_{eff}:

$$\mu_{eff} = 2.828\sqrt{\chi \cdot T} = 2.828\sqrt{\chi} \cdot \sqrt{T} = const \cdot \sqrt{T}$$

$$\text{for } \chi_{TIP} = 600 \cdot 10^{-6} \text{cm}^3\text{mol}^{-1}$$

$$\mu_{eff} = 2.828\sqrt{600 \cdot 10^{-6} \text{cm}^3\text{mol}^{-1} \cdot T} = 1.2\,\mu_B \text{ bei } 300\,\text{K}$$

2.7. Complete treatment of mononuclear systems

$$\hat{H} = \mu_B g_x H_x \hat{S}_x + \mu_B g_y H_y \hat{S}_y + \mu_B g_z H_z \hat{S}_z$$
$$+ D\left(\hat{S}_z^2 - \tfrac{1}{3}\left(S(S+1)\right)\right) + E(\hat{S}_x^2 - \hat{S}_y^2)$$

♦ diagonalization of the spin Hamiltonian matrix

  ⇒ energies

  ⇒ plug into equation for χ_m

  ⇒ fit parameters to experimental χ_m vs. T

  ⇒ interprete spin Hamiltonian parameters to gain insight into the electronic and thus geometric structure of the complex

♦ magnetization measurements: effects of zero-field splitting

  example: $S = 5/2$, $g = 2.00$
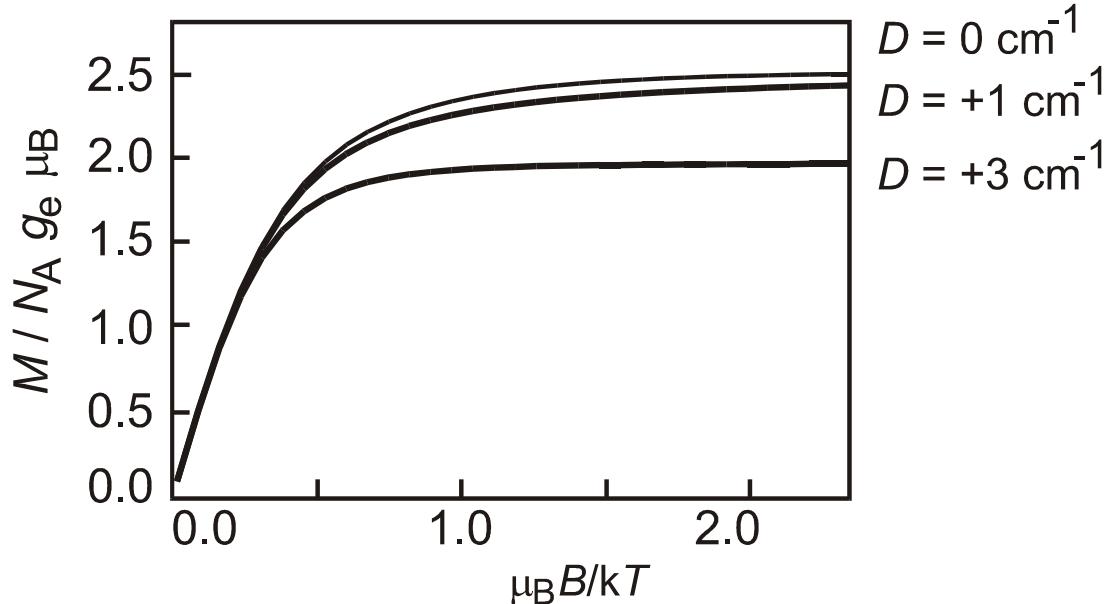
$D = 0$ corresponds to Brillouin function

♦ variable field - variable temperature (VTVH) measurements
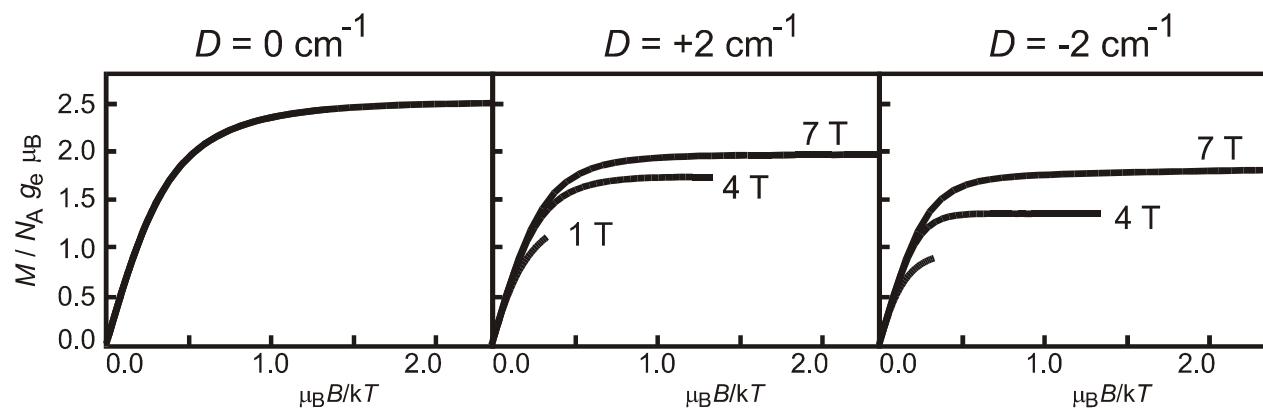
⟹ in some cases, not only magnitude but also sign of zero-field splitting accessible by bulk magnetization measurement

3. Intramolecular exchange couplings
3.1. Introduction

ex.: $[Cu^{II}_2(OAc)_4(H_2O)_2]$

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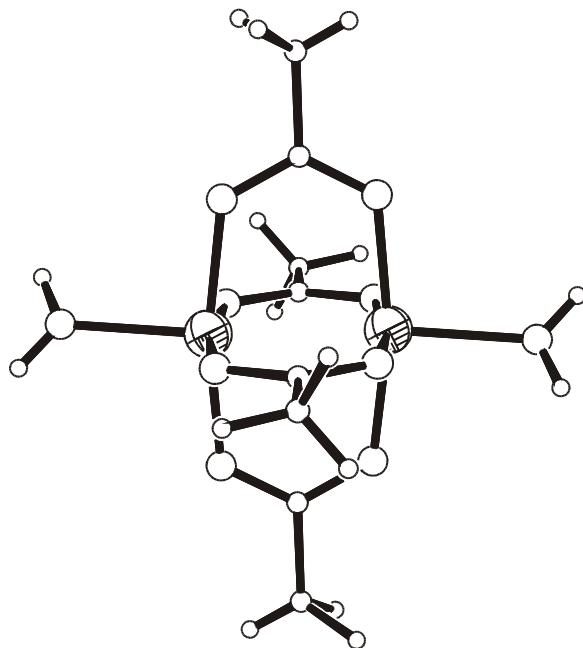
$$\mu_{eff} = g\sqrt{S_1(S_1+1) + S_2(S_2+1)} = 2.58 \text{ for } \quad g = 2.11$$

but experiment:
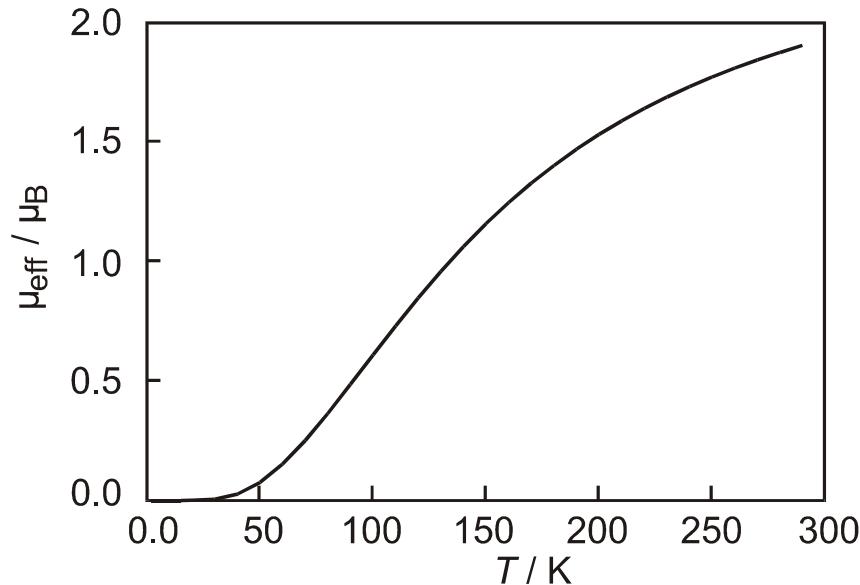
at 0 K no magnetization →   must have diamagnetic ground state

antiferromagnetic
coupling:

ferromagnetic
coupling:

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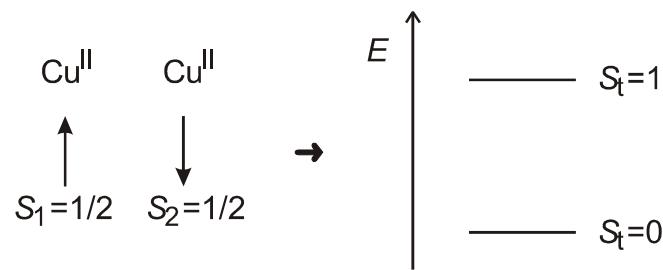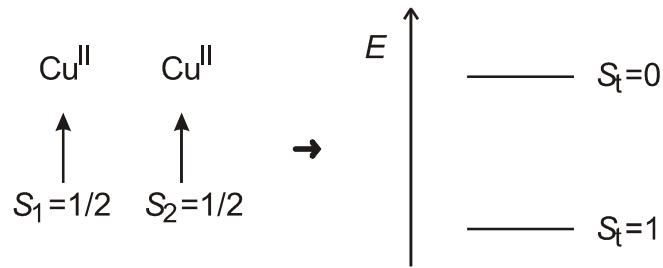
3.2. Heisenberg-Dirac-van Vleck (HDvV) Operator

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

$J < 0$: antiferromagnetic $J > 0$: ferromagnetic

$$S_t = S_1 + S_2, S_1 + S_2 - 1, ..., |S_1 - S_2|$$

$$\mathbf{S}_t = \mathbf{S}_1 + \mathbf{S}_2$$

$$\mathbf{S}_t{}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 = \mathbf{S}_1{}^2 + \mathbf{S}_2{}^2 + 2\mathbf{S}_1\mathbf{S}_2$$

$$\mathbf{S}_1\mathbf{S}_2 = \tfrac{1}{2}\left(\mathbf{S}_t{}^2 - \mathbf{S}_1{}^2 - \mathbf{S}_2{}^2\right) \qquad \text{with} \qquad \mathbf{S}^2|S\rangle = S(S+1)|S\rangle$$

$$\hat{H} = -2J\mathbf{S}_1\mathbf{S}_2 = -J\left(\mathbf{S}_t{}^2 - \mathbf{S}_1{}^2 - \mathbf{S}_2{}^2\right)$$

$$\hat{H}|S_t, S_1, S_2\rangle = -J\left(\mathbf{S}_t{}^2 - \mathbf{S}_1{}^2 - \mathbf{S}_2{}^2\right)|S_t, S_1, S_2\rangle = E|S_t, S_1, S_2\rangle$$

$$E(S_t) = -J\left[S_t(S_t+1) - S_1(S_1+1) - S_2(S_2+1)\right]$$
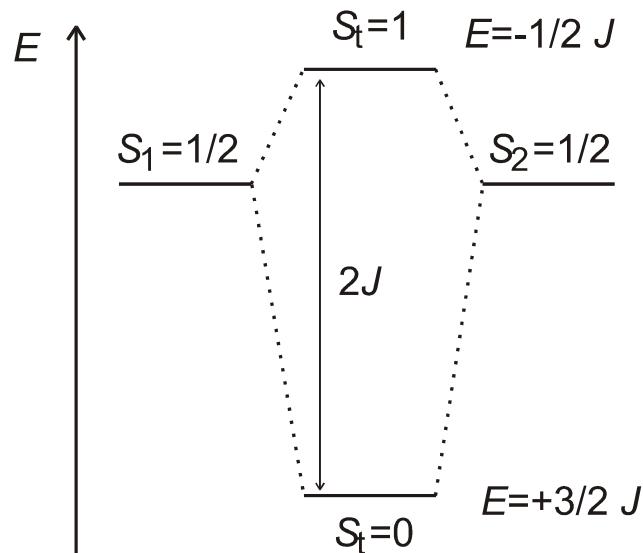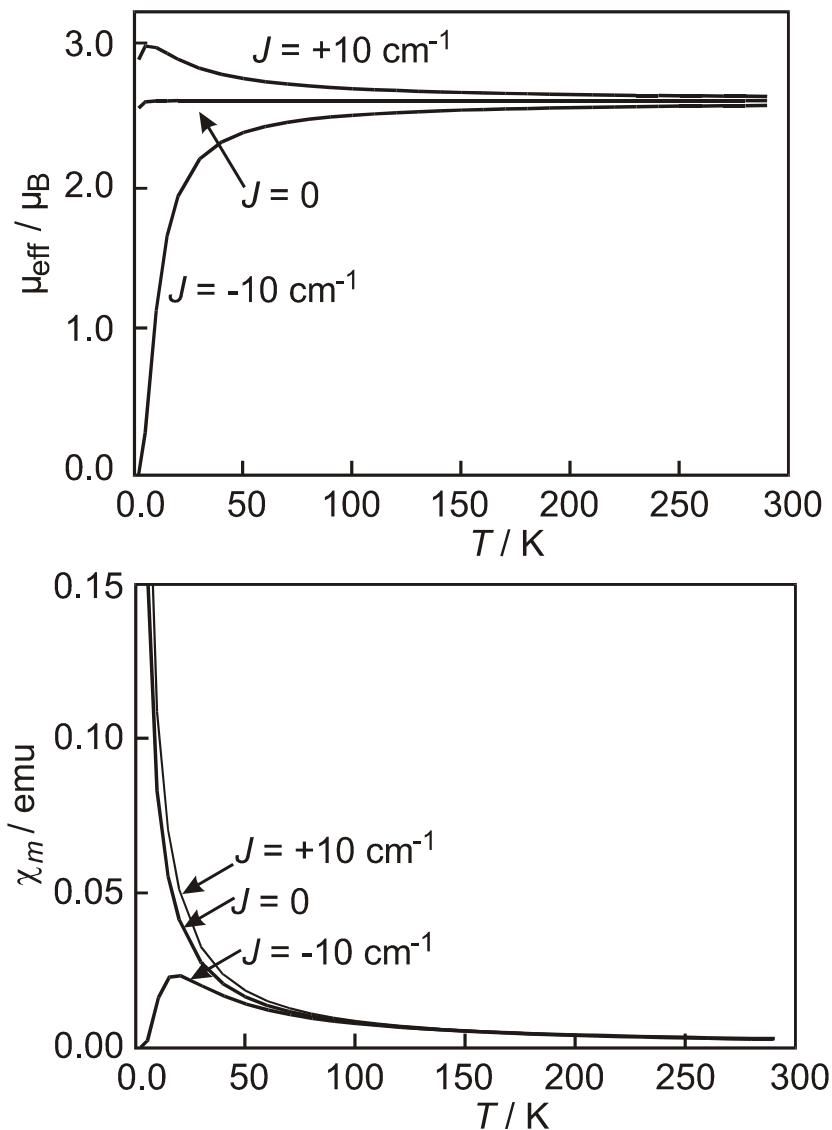
♦ General Spin-System

$$E(S_t) = -J[S_t(S_t + 1)] = -J[S_t^2 + S_t]$$

$$E(S_t + 1) = -J[(S_t + 1)(S_t + 2)] = -J[(S_t^2 + 3S_t + 2)]$$

$$\Delta E = E(S_t + 1) - E(S_t) = -J[S_t^2 + S_t] - (-J)[(S_t^2 + 3S_t + 2)] =$$

$$= -J[S_t^2 + S_t - S_t^2 - 3S_t - 2] = -J[-2S_t - 2] = -2J(S_t + 1)$$

Lande Interval-Regel

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   }   splitting is not equidistant, but increases with increasing S_T

♦ $S_1 = 5/2$ and $S_2 = 5/2$ (Fe^{III} - Fe^{III}) spin system

$$S_t = \frac{5}{2} + \frac{5}{2}, \frac{5}{2} + \frac{5}{2} - 1, ..., \left|\frac{5}{2} - \frac{5}{2}\right|$$
$$= 5, 4, 3, 2, 1, 0$$

$$E(S_t) = -J\left[S_t(S_t + 1)\right]$$

$$E(S_t = 0) = -J\left[0(0 + 1)\right] = 0$$
$$E(S_t = 1) = -J\left[1(1 + 1)\right] = -2J$$
$$E(S_t = 2) = -J\left[2(2 + 1)\right] = -6J$$
$$E(S_t = 3) = -J\left[3(3 + 1)\right] = -12J$$
$$E(S_t = 4) = -J\left[4(4 + 1)\right] = -20J$$
$$E(S_t = 5) = -J\left[5(5 + 1)\right] = -30J$$

-30 *J* —— S_t=5

-20 *J* —— S_t=4

E

-12 *J* —— S_t=3

-6 *J* —— S_t=2

-2 *J* —— S_t=1

0 —— S_t=0

spin ladder

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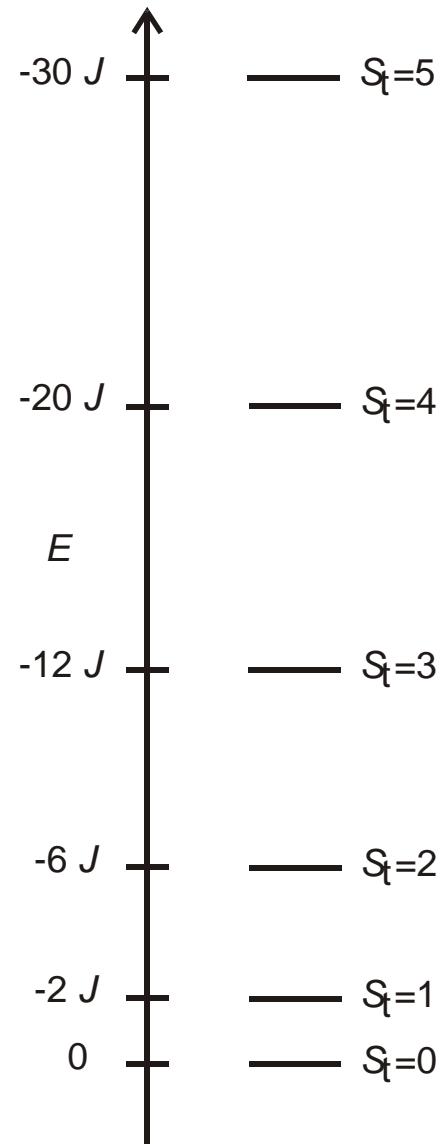
♦ ex. Fe^{III} - O - Fe^{III} dimers   (g = 2.00)
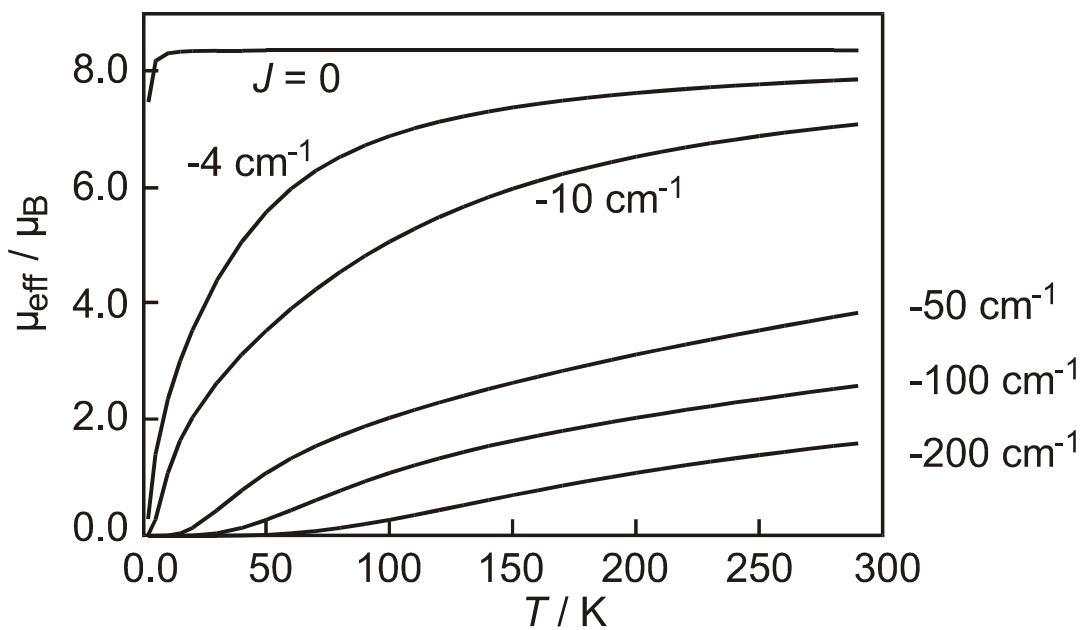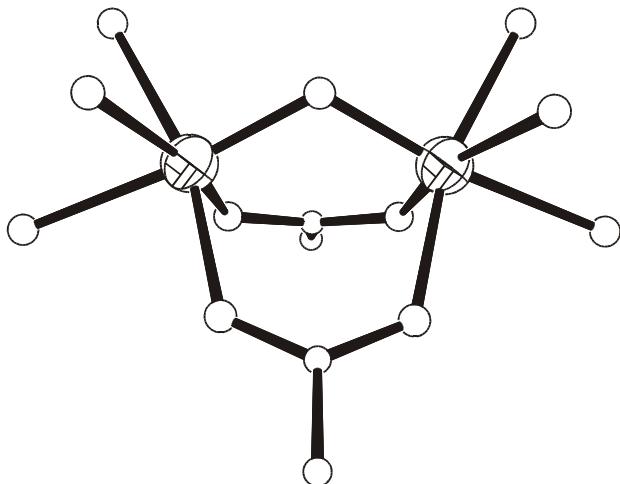
- OH_2 bridge $J \sim$ -2 cm^{-1}
- OH^- bridge $J \sim$ -10 cm^{-1}
- O^{2-} bridge $J \sim$ -100 cm^{-1}

Magnetism - Structure - Relationship

Why ? ⇒ mechanism of interaction

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3.3. Bleaney-Bowers Equations

B. Bleaney, K. D. Bowers, *Proc. R. Soc. Lond.* **1952**, *A214*, 451

Goal: equation for calculation of χ_m as function of *J* and *T*,
         simulation of measured temperature-dependent
         susceptibilities by using e. g. Excel

van Vleck equation: note: $\dfrac{H}{kT} \langle\langle 1$!!!

e.g.: $Cu^{II}Cu^{II}$ dimer
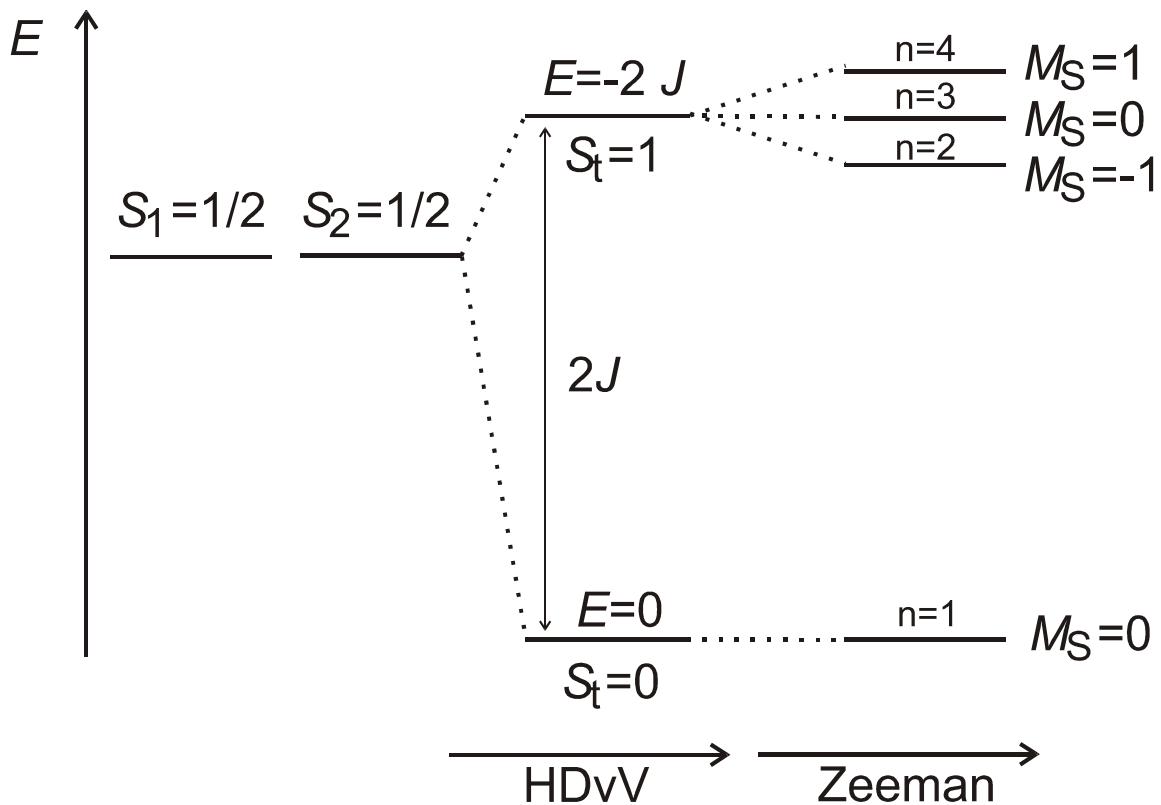
$$E_n = E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2$$

$$\chi_m = N_A \cdot \frac{\sum\limits_n \left[\left(\dfrac{E_n^{(1)^2}}{kT} - 2E_n^{(2)} \right) \cdot \exp\left(-\dfrac{E_n^{(0)}}{kT} \right) \right]}{\sum\limits_n \exp\left(-\dfrac{E_n^{(0)}}{kT} \right)}$$

$$E_{n=1} = 0 + 0 \cdot \mu_B gB \qquad\qquad E^{(0)}_{n=1} = 0 \qquad\qquad E^{(1)}_{n=1} = 0$$

$$E_{n=2} = -2J - 1 \cdot \mu_B gB \qquad\qquad E^{(0)}_{n=2} = -2J \qquad E^{(1)}_{n=2} = -\mu_B g$$

$$E_{n=3} = -2J - 0 \cdot \mu_B gB \qquad\qquad E^{(0)}_{n=3} = -2J \qquad E^{(1)}_{n=3} = 0$$

$$E_{n=4} = -2J + 1 \cdot \mu_B gB \qquad\qquad E^{(0)}_{n=4} = -2J \qquad E^{(1)}_{n=4} = \mu_B g$$

$$\chi_m = N_A \cdot \frac{\left[\left(\dfrac{0}{kT} \right) \cdot \exp\left(-\dfrac{0}{kT} \right) \right] + \left[\left(\dfrac{\mu_B^2 g^2}{kT} \right) \cdot \exp\left(\dfrac{2J}{kT} \right) \right] + \left[\left(\dfrac{0}{kT} \right) \cdot \exp\left(\dfrac{2J}{kT} \right) \right] + \left[\left(\dfrac{\mu_B^2 g^2}{kT} \right) \cdot \exp\left(\dfrac{2J}{kT} \right) \right]}{\exp\left(-\dfrac{0}{kT} \right) + \exp\left(\dfrac{2J}{kT} \right) + \exp\left(\dfrac{2J}{kT} \right) + \exp\left(\dfrac{2J}{kT} \right)}$$

$$\chi_m = N_A \cdot \frac{\left[\left(\dfrac{\mu_B^2 g^2}{kT} \right) \cdot \exp\left(\dfrac{2J}{kT} \right) \right] + \left[\left(\dfrac{\mu_B^2 g^2}{kT} \right) \cdot \exp\left(\dfrac{2J}{kT} \right) \right]}{1 + 3 \cdot \exp\left(\dfrac{2J}{kT} \right)}$$

$$\chi_m = \frac{N_A \mu_B^2 g^2}{kT} \cdot \frac{\left[2 \cdot \exp\left(\dfrac{2J}{kT} \right) \right]}{1 + 3 \cdot \exp\left(\dfrac{2J}{kT} \right)}$$

Bleaney-Bower equation for $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ system; other spin systems: C.J.O´Conner, *Prog. Inorg. Chem.* **1982**, *29*, 203-283

4. Super Exchange Mechanism
## 4.1. Fundamental Considerations

interactions between paramagnetic centers

<u>through space</u>　　　　　　<u>through bonds</u>
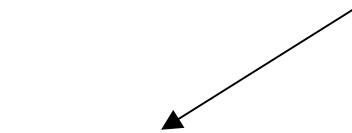
**dipolar spin-spin
interactions**
(magnetic interaction,
relative small, r^{-3}, < 1 cm^{-1})

**electrostatic
interactions**
(not a magnetic interaction
relative large, 1 – 200 cm^{-1})
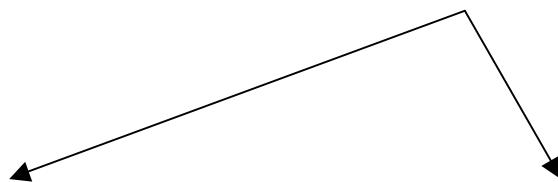
super exchange
through overlap
of metal d-orbitals
with orbitals
of the bridging ligands

direct exchange
direct overlap
of metal d-orbitals

model compound: $Cu^{II}(A)$ $Cu^{II}(B)$

ψ_A ψ_B
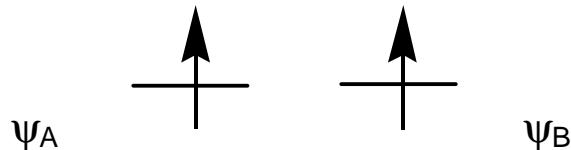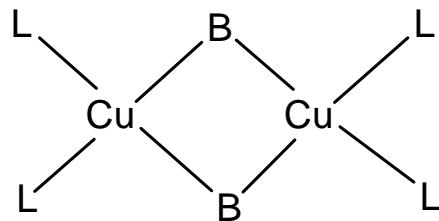
active orbitals (contain some ligand character)

neglect all other orbitals (active orbital approximation)

ψ_A ψ_B
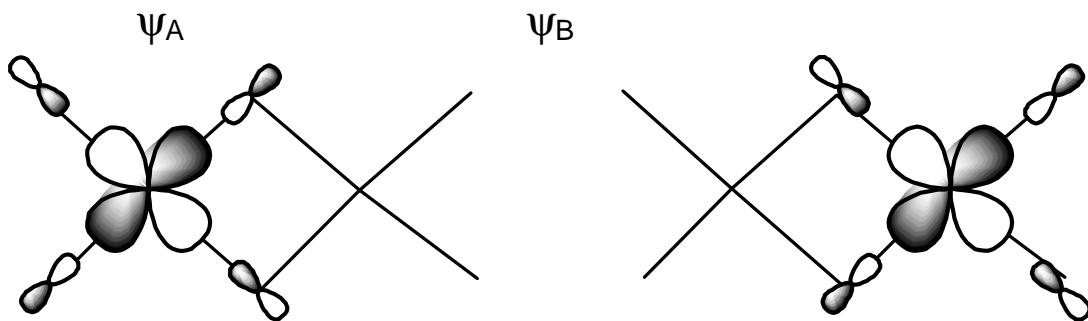
4.2. Anderson Model

orthogonalization of the two localized orbitals ψ_A and ψ_B:

a   b
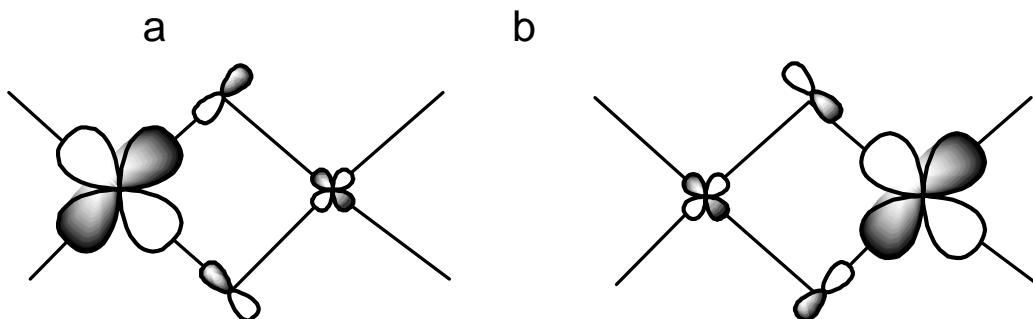
- **ground state configuration**:

$$a \underline{\quad\uparrow\quad} \quad\quad \underline{\quad\uparrow\quad} b$$

turn on electron-electron Coulomb repulsion:

$$a^1b^1 \quad \xrightarrow{\text{e}^- \text{-e}^-} \quad \begin{array}{c} \underline{\qquad}\,^1GC \\[3em] \underline{\qquad}\,^3GC \end{array} \quad \updownarrow\ 2\,k$$
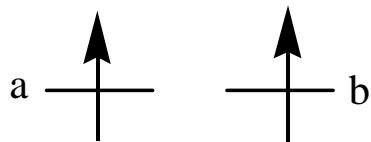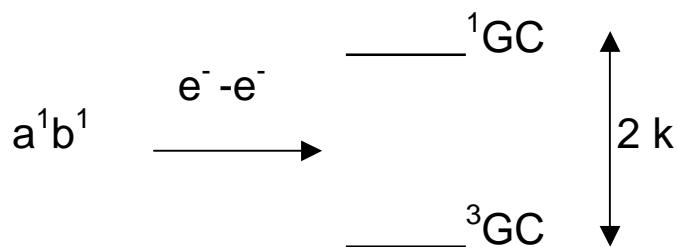
"Hund's in the molecule": ferromagnetic interaction as in O_2

- **charge transfer excited configurations**
  excited configurations by intramolecular electron transfer

$$a \underline{\quad\uparrow\downarrow\quad} \quad\underline{\qquad}\, b \qquad\qquad a\underline{\qquad} \quad \underline{\quad\uparrow\downarrow\quad} b$$

$$\text{Cu}^\text{I} \qquad \text{Cu}^\text{III} \qquad\qquad\qquad \text{Cu}^\text{III} \qquad \text{Cu}^\text{I}$$

  – these configurations are – of course – at higher energy
  – there are only singlet configurations
  – turn on electron-electron Coulomb repulsion
  – symmetrize
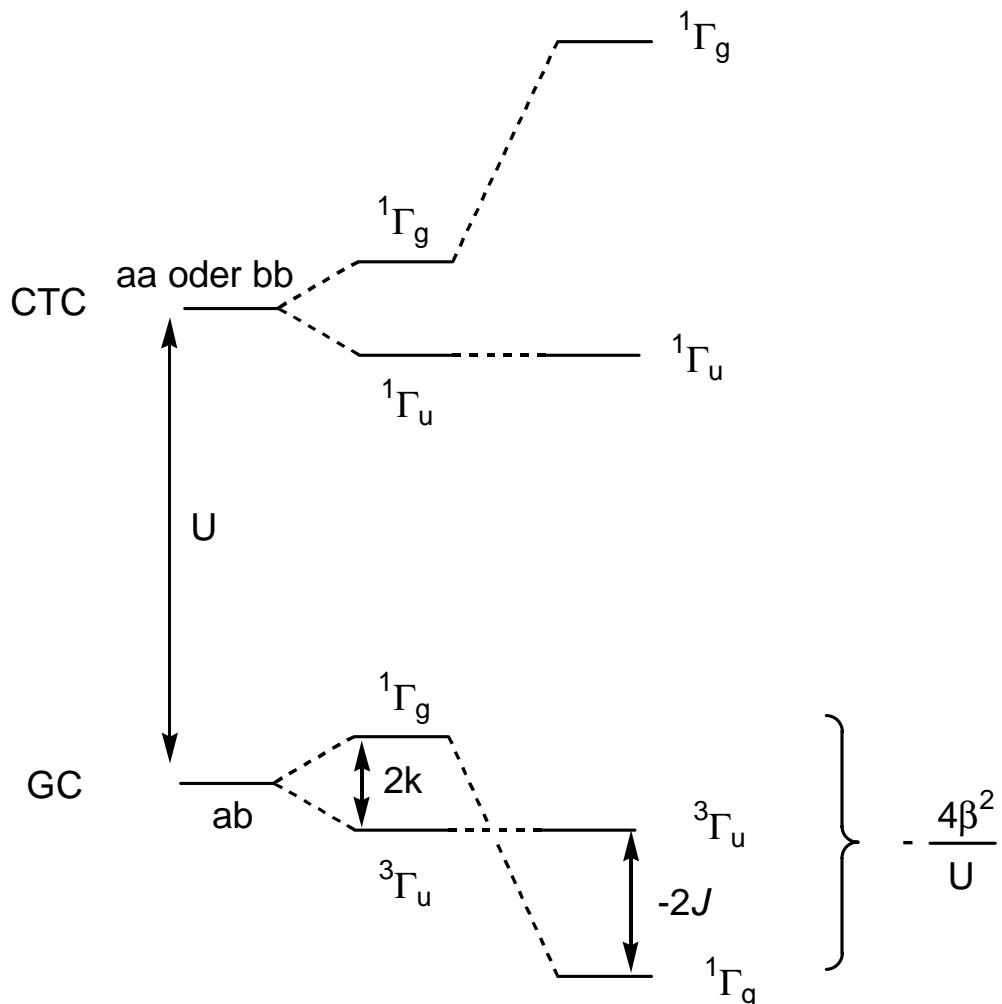
$$J = J_{ferro} + J_{antiferro}$$

$$J = 4k - \frac{4\beta^2}{U}$$

potential exchange   *kinetic exchange*

β: transfer intergral: transfer of an electron from one site to the other *through bonds*

$$\beta = \left\langle \Psi_A \left| \hat{H} \right| \Psi_B \right\rangle \quad mit \quad \Psi_A : A^{\bullet} - B$$

$$\Psi_B : A - B^{\bullet}$$

➢ the stronger the bonds, the larger β, the larger the antiferromagnetic contribution

$$\beta \propto -S$$

S: overlap integral

➢ are the magnetic orbitals orthogonal $\rightarrow S = 0 \rightarrow \beta = 0$

only ferromagnetic contribution remains

4.3. Goodenough-Kanomori-Rules

1. The overlap of magnetic orbitals of two metal centers with an overlap integral $S \neq 0$ yields an antiferromagnetic interaction.

2. Are the overlapping magnetic orbitals orthogonal, the overlap $S = 0$ and the interaction is ferromagnetic.

3. The non-orthogonal overlap of a magnetic orbital of one metal center with a filled or empty orbital of the other metal center yields a ferromagnetic interaction

4.4. Kahn's Model of the Natural Magnetic Orbitals NMO's

− exchange interactions represents the limit of weak chemical bonding

− the chemist like to explain chemical bonding by the overlap of localized orbitals

− orthogonalized magnetic orbitals are not localized

natural magnetic orbitals:

$$A \underline{\hspace{1cm}} X \underline{\hspace{1cm}} B$$

$$\downarrow$$

$$A \underline{\hspace{1cm}} X \qquad\qquad X \underline{\hspace{1cm}} B$$

NMO a is the singly occupied MO in the AX fragment

NMO b is the singly occupied MO in the XB fragment
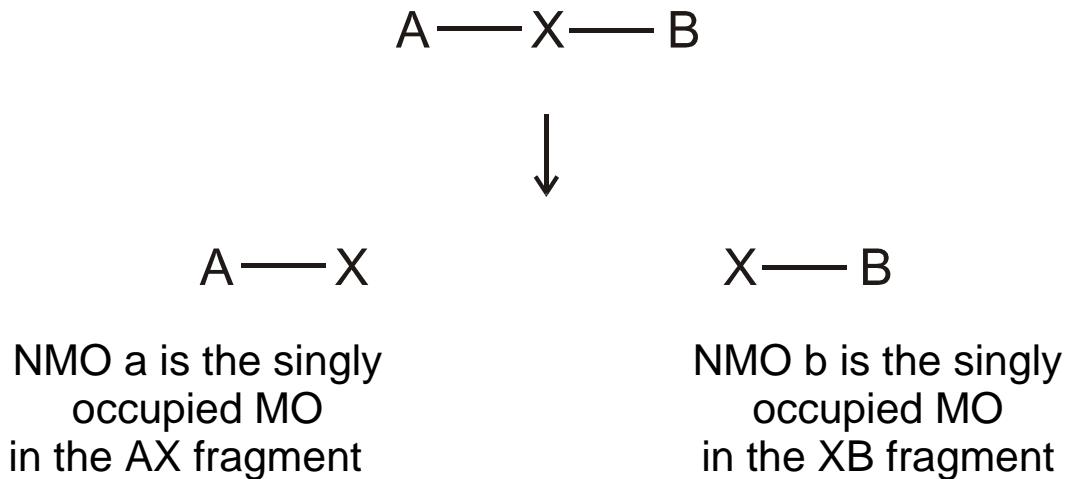
Exchange coupling arises of overlap of NMO's:
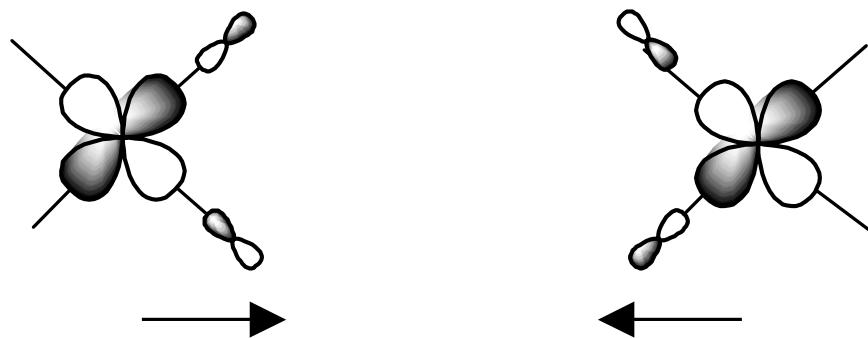
$$J = 2k + 4\beta S$$

– ET excited states of Anderson's model energetically too high (e.g. $Cu^{I}Cu^{III}$, $Fe^{II}Fe^{IV}$); here: ground configuration phenomenon

– strong antiferromagnetic coupling would need lower energy excited states

4.5. Examples
Fe-OH$_n$-Fe systems

1.8 Å	2.0 Å	2.2 Å

O — Fe, Fe

H — O, Fe, Fe

H$_2$ — O, Fe, Fe

$J =$ -100 cm^{-1} -10 cm^{-1} -2 cm^{-1}

Fe 3d   Fe 3d   Fe 3d

O 2p   O 2p   O 2p
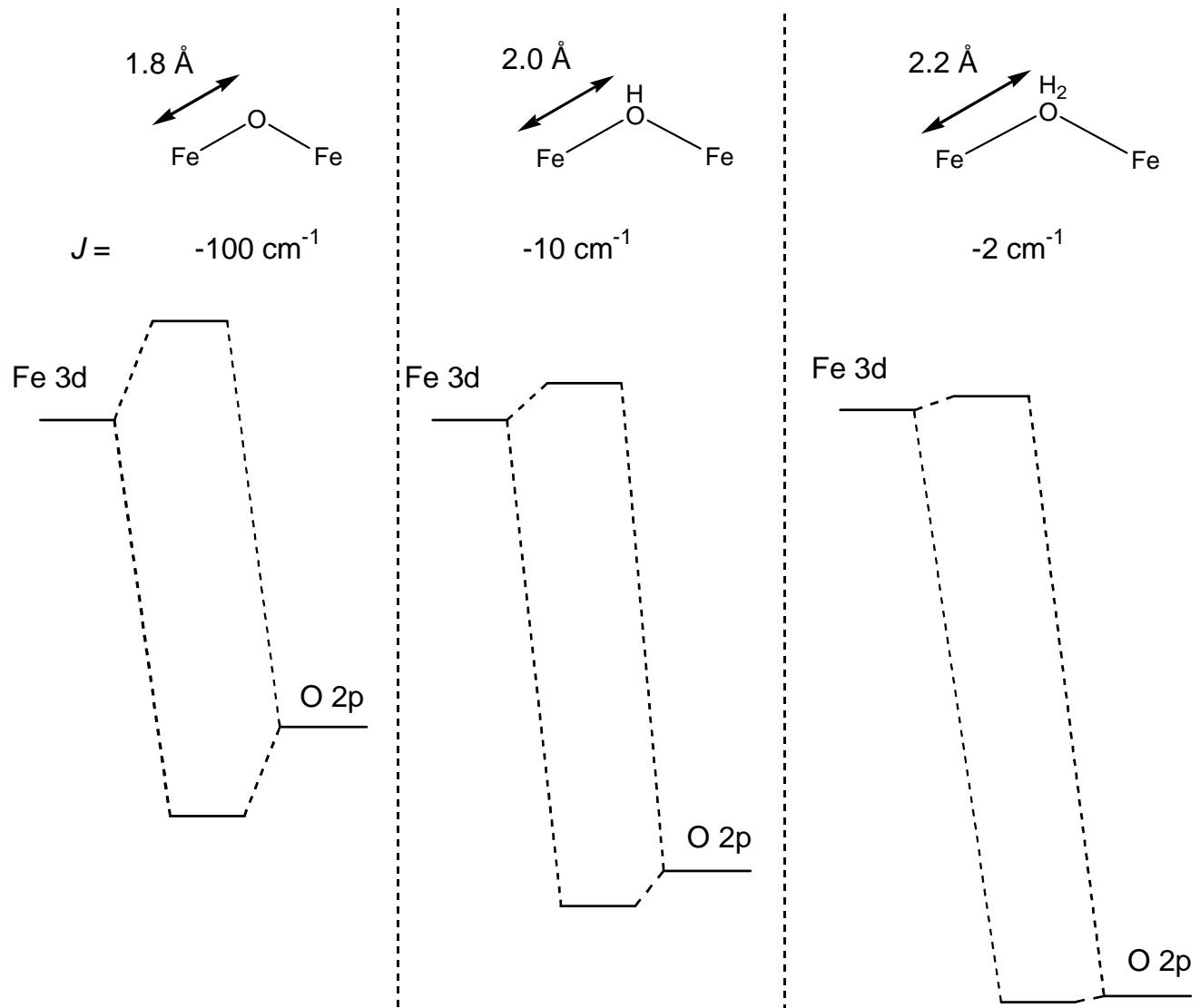
Cu(OH)$_2$Cu   Hatfield and Hodgson

magneto-structural correlation
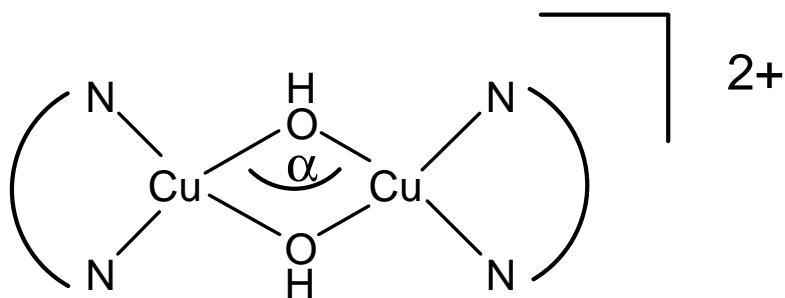
Cu(OH)$_2$Cu complex	Cu-O-Cu / °	J / cm^{-1}
[Cu(bipy)OH]$_2$(NO$_3$)$_2$	95.5	+172
[Cu(bipy)OH]$_2$(ClO$_4$)$_2$	96.6	+93
[Cu(bipy)OH]$_2$(SO$_4$)·5H$_2$O	97	+49
β-[Cu(dmaep)OH]$_2$(ClO$_4$)$_2$	98.4	-2.3
[Cu(eaep)OH]$_2$(ClO$_4$)$_2$	98.8; 99.5	-130
[Cu(2miz)OH]$_2$(ClO$_4$)$_2$·2H$_2$O	99.4	-175
α-[Cu(dmaep)OH]$_2$(ClO$_4$)$_2$	100.4	-200
[Cu(tmen)OH]$_2$(ClO$_4$)$_2$	102.3	-306
[Cu(tmen)OH]$_2$(NO$_3$)$_2$	101.9	-367
α-[Cu(teen)OH]$_2$(ClO$_4$)$_2$	103.0	-410
β-[Cu(teen)OH]$_2$(ClO$_4$)$_2$	103.7	-469
[Cu(tmen)OH]$_2$Br$_2$	104.1	-509
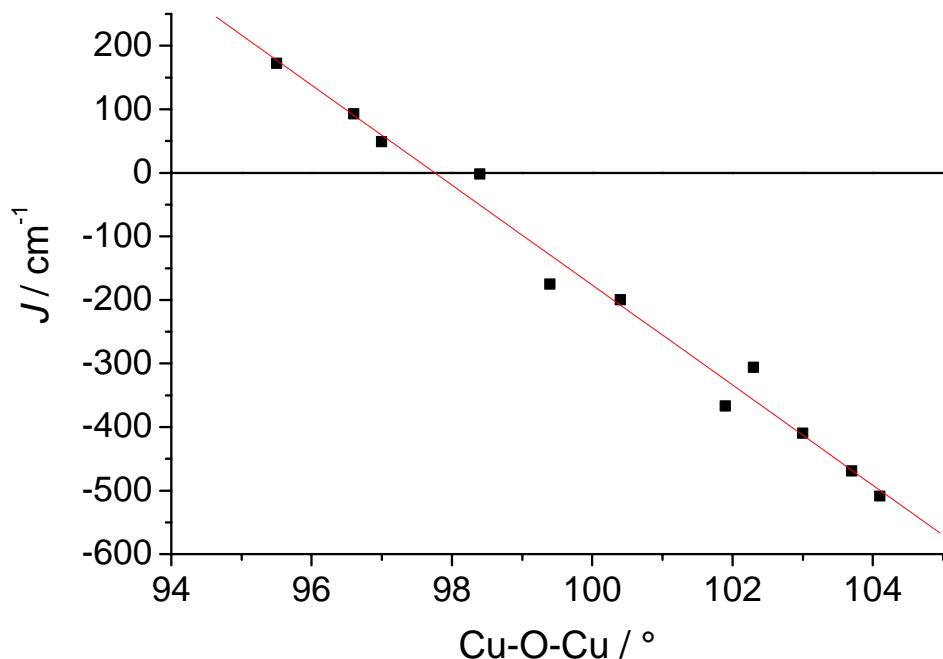
$$J = -74\,\alpha + 7270$$

$J = 0$ for $\alpha = 97.5°$

$J < 0$ for $\alpha > 97.5°$ antiferromagnetic

$J > 0$ for $\alpha < 97.5°$ ferromagnetic
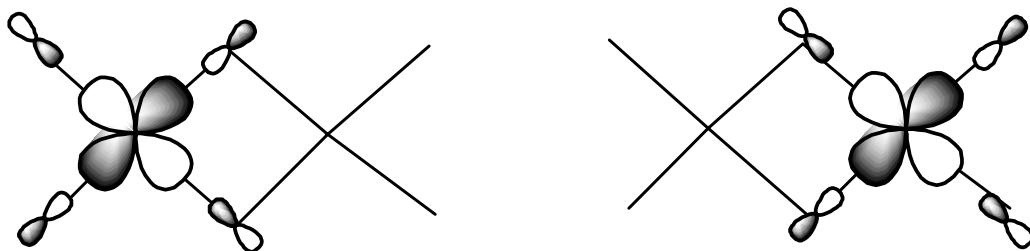
$$J = 2k + 4\beta S$$

$\alpha = 90°$ $4\beta S = 0$ $J = 2k$

$\alpha \uparrow$ $\Rightarrow$ $4\beta S \uparrow$ $\Rightarrow$ stronger antiferromagnetic contribution

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