Workshop in Magnetochemistry
Molecular Magnetism (DFG-SPP 1137)
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Foundations

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Contents

1 Magnetic quantities

- The legal SI units are not generally accepted. The CGS/emu system is still widely used in magnetochemistry. Therefore, use magnetic quantities which are independent of the two systems, e. g., μ_{eff} or μ_{eff}^2 instead of $\chi_{mol}T$
- do not mix the systems, e. g., use G (gauss) instead of T (tesla) in the CGS/emu system
- use $\boldsymbol{B}_0 = \mu_0\boldsymbol{H}$ in graphical representations (conversion factor 10^{-4} T/Oe)

Table 1: Definitions, units and conversion factors [1, 2]

	quantity	SI		CGS/emu
μ_0	permeability of a vacuum	$4\pi/10^7$ Vs/(Am)		1
$\boldsymbol{B}$	magnetic flux density	$\mathrm{T} = \mathrm{Vs/m^2}$ 1 T	 $\widehat{=}$	$\mathrm{G} = (\mathrm{erg/cm^3})^{1/2}$ 10^4 G
$\boldsymbol{H}^a$	magnetic field strength	A/m 1 A/m	 $\widehat{=}$	Oe $(4\pi/10^3)$ Oe
$\boldsymbol{M}$	magnetisation	$\boldsymbol{B} = \mu_0(\boldsymbol{H}+\boldsymbol{M})$ A/m 1 A/m	 $\widehat{=}$	$\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{M}$ G 10^{-3} G
$\boldsymbol{m}$	magnetic dipole moment	$\boldsymbol{m} = \boldsymbol{M}V$ $\mathrm{Am^2}$ 1 $\mathrm{Am^2}$	 $\widehat{=}$	$\boldsymbol{m} = \boldsymbol{M}V$ G cm^3 10^3 G cm^3
μ_B	Bohr magneton	$e\hbar/(2m_e)$ 9.27402×10^{-24} $\mathrm{Am^2}$	 $\widehat{=}$	$e\hbar/(2m_e)$ 9.27402×10^{-21} G cm^3
σ	magnetic dipole moment per unit mass^c	$\sigma = M/\rho$ ^{b} $\mathrm{Am^2/kg}$ 1 $\mathrm{Am^2/kg}$	 $\widehat{=}$	$\sigma = M/\rho$ G cm^3/g 1 G cm^3/g
M_{mol}	molar magnetisation^e	$M_{mol} = M\mathrm{M_r}/\rho$ ^{d} $\mathrm{Am^2/mol}$ 1 $\mathrm{Am^2/mol}$	 $\widehat{=}$	$M_{mol} = M\mathrm{M_r}/\rho$ G cm^3/mol 10^3 G cm^3/mol
μ_m^s	atomic magnetic saturation moment	$\mu_m^s/\mu_B = M_{mol}^s/(N_A\mu_B)$ ^{f} μ_B		$\mu_m^s/\mu_B = M_{mol}^s/(N_A\mu_B)$ μ_B

[a] If $\boldsymbol{B}_0 = \mu_0\boldsymbol{H}$ is used instead of $\boldsymbol{H}$, e. g., in graphs, the conversion factor is 10^{-4} T/Oe.
[b] ρ specific density.
[c] Specific magnetisation; σ^s specific saturation magnetisation.
[d] $\mathrm{M_r}$ molar mass.
[e] M_{mol}^s molar saturation magnetisation.
[f] N_A Avogadro constant.

Table 1: Definitions, units and conversion factors [1, 2] (cont.)

quantity		SI		CGS/emu
χ	magnetic volume susceptibility	$\boldsymbol{M} = \chi \boldsymbol{H}$		$\boldsymbol{M} = \chi \boldsymbol{H}$
		1		1
		1	$\widehat{=}$	$1/(4\pi)$
χ_g	magnetic mass susceptibility	$\chi_g = \chi/\rho$		$\chi_g = \chi/\rho$
		$\mathrm{m^3/kg}$		$\mathrm{cm^3/g}$
		$1\,\mathrm{m^3/kg}$	$\widehat{=}$	$10^3/(4\pi)\,\mathrm{cm^3/g}$
χ_{mol}	magnetic molar susceptibility	$\chi_{mol} = \chi \mathrm{M}_r/\rho$		$\chi_{mol} = \chi \mathrm{M}_r/\rho$
		$\mathrm{m^3/mol}$		$\mathrm{cm^3/mol}$
		$1\,\mathrm{m^3/mol}$	$\widehat{=}$	$4\pi/10^6\,\mathrm{cm^3/mol}$
μ_{eff}	effective Bohr magneton number [3]	$[3k_B/(\mu_0 N_A \mu_B^2)]^{1/2}[\chi_{mol}T]^{1/2}$ [a]		$[3k_B/(N_A \mu_B^2)]^{1/2}[\chi_{mol}T]^{1/2}$
		1		1
		1	$\widehat{=}$	1

[a] k_B Boltzmann constant.

2 Magnetisation and magnetic susceptibility

magnetic flux density in vacuo — in matter

$$\boldsymbol{B} = \mu_0 \boldsymbol{H} \qquad \boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M}) \tag{1}$$

magnetisation

$$\boldsymbol{M} = \chi \boldsymbol{H} \tag{2}$$

magnetic susceptibility

magnetic volume susceptibility χ

magnetic mass susceptibility $\chi_g = \chi/\rho$

magnetic molar susceptibility

$$\chi_{mol} = \chi_g \mathrm{M}_r \tag{3}$$

substance class		range	
diamagnets	$\chi < 0$	$-10^{-4} \ldots -10^{-6}$	closed shell atoms
vacuum	$\chi = 0$		
paramagnets	$\chi > 0$	$10^{-2} \ldots 10^{-5}$	open shell atoms

Diamagnetism

(i) $\chi < 0$ and $\boldsymbol{M} < 0$ owing to small additional currents attributable to the precession of electron orbits about the applied magnetic field (shown by all substances);
(ii) usually independent of both T and B for purely diamagnetic materials (closed shell systems);
(iii) allowed for as diamagnetic correction in the evaluation of experimental susceptibility data of open shell systems.

Paramagnetism

(i) $\chi > 0$ and $\boldsymbol{M} > 0$ owing to net spins and orbital angular momentum polarized in direction of the applied field;
(ii) observed in various forms, differing in magnitude and dependency on T and B:
CURIE *paramagnetism*: inverse dependency on T, independence on B at weak applied fields, but inverse dependency at strong fields (paramagnetic saturation, see Figure 1) where $B(\alpha) = M_{mol}/M_{mol}^{\infty}$ with $M_{mol}^{\infty} = N_A\, g_J\, J\, \mu_B$;
temperature independent paramagnetism: weak forms of paramagnetism, called PAULI paramagnetism (of conduction electrons observed in metals) and VAN VLECK paramagnetism (TIP, second order effect involving mixing with the first excited multiplet by the applied field; example: Eu^{3+}).

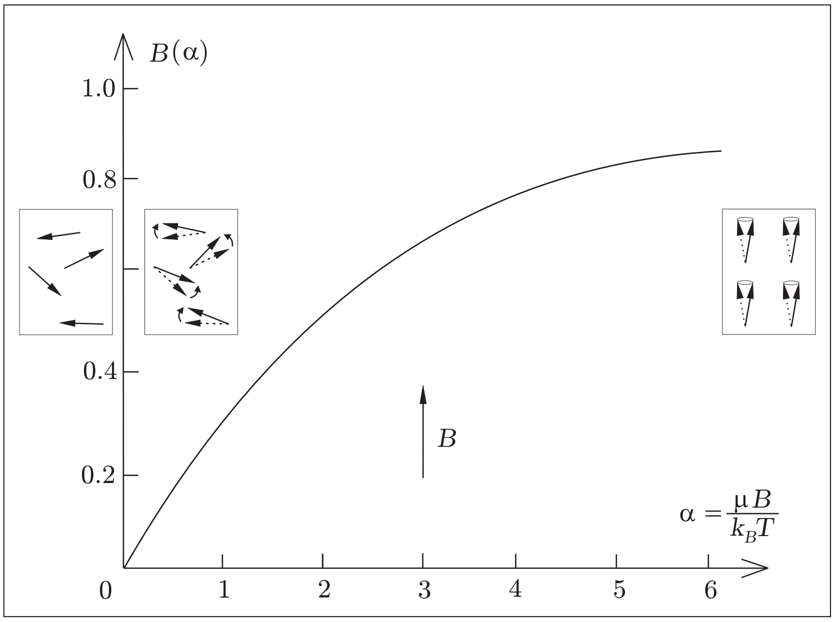


Fig. 1: BRILLOUIN function $B(\alpha)$; inserts: magnetic dipoles (left: randomly distributed, $B = 0$; middle: weakly polarised, weak B, high T; right: completely aligned, strong B, low T)

CURIE limit: $k_BT \gg \mu B$ paramagnetic saturation: $k_BT \ll \mu B$

3 Paramagnetism

3.1 CURIE law

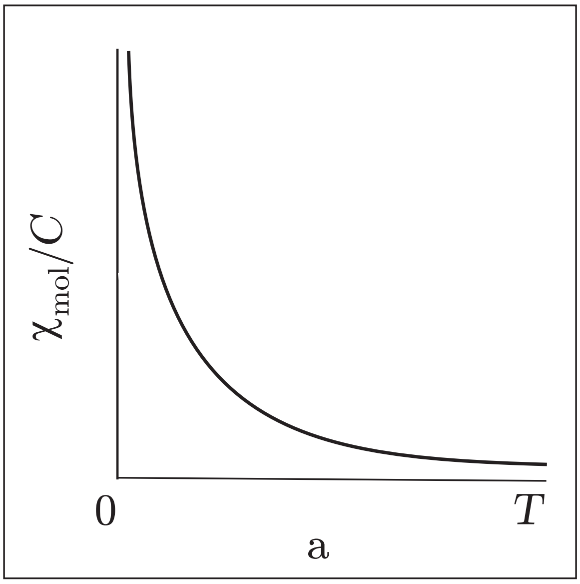
$$\boxed{\chi_{mol} = \frac{M_{mol}}{H} = \frac{C}{T} \quad \text{where} \quad C = \mu_0 \frac{N_A \mu^2}{3k_B}} \tag{4}$$

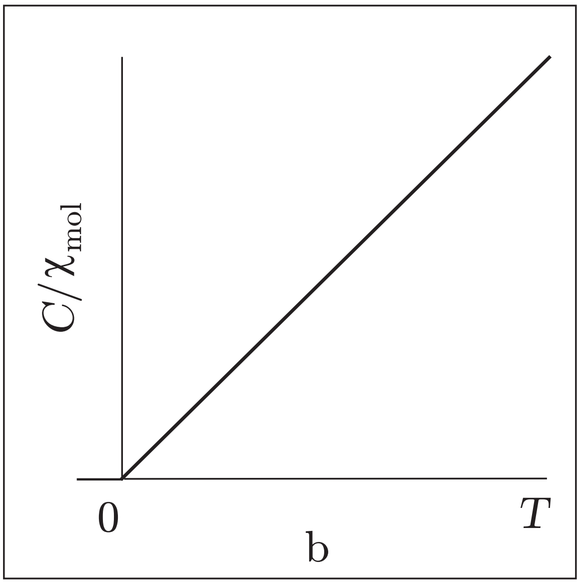
C: CURIE constant; μ: permanent magnetic moment of an atom

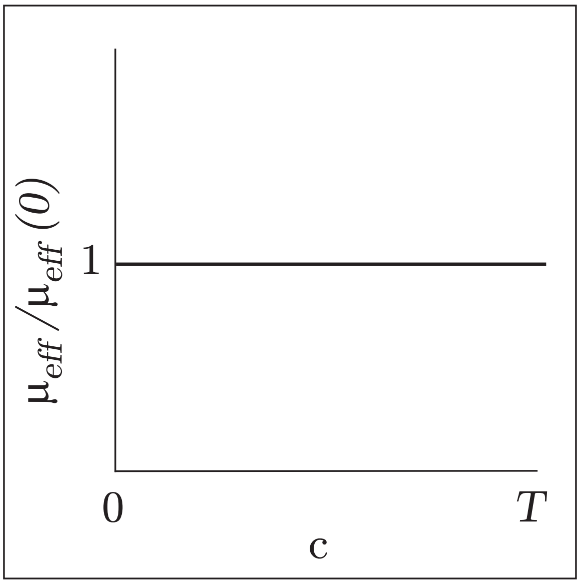
Preconditions for CURIE behaviour, examples

- magnetically isolated centres

- thermally isolated ground state $\longrightarrow$ temperature independent C







CURIE behaviour (in reduced magnetic quantities χ_{mol}/C and $\mu_{eff}/\mu_{eff}(0)$
(C and $\mu_{eff}(0)$ refer to the free ion)

Fig. 2 a: variation χ_{mol} *vs.* T
Fig. 2 b: variation χ_{mol}^{-1} *vs.* T
Fig. 2 c: variation μ_{eff} *vs.* T

$$\boxed{\mu = g\sqrt{S(S+1)}\,\mu_B \qquad \text{spin-only formula}} \tag{5}$$

$Gd_2(SO_4)_3 \cdot 8\,H_2O$ and $(NH_4)_2Mn(SO_4)_2 \cdot 6\,H_2O$ with
Gd^{3+} [$4f^7$] (ground state $^8S_{7/2}$, $S = 7/2$, $\mu = 7.94\,\mu_B$)
Mn^{2+} [$3d^5$] (ground state $^6A_1$, $S = 5/2$, $\mu = 5.91\,\mu_B$)

3.2 Free lanthanide ions and HUND's rules

$$\boxed{\mu = g_J \sqrt{J(J+1)}\,\mu_B} \qquad \text{except} \quad 4\text{f}^4, 4\text{f}^5, 4\text{f}^6 \quad \text{systems} \tag{6}$$

with LANDÉ factor

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{7}$$

S, L, J correspond to the total spin angular momentum, the total orbital angular momentum and the total angular momentum, respectively, of the ground state.

The 4f electrons of free Ln ions are influenced by interelectronic repulsion H_{ee} (splitting energy $10^4\,\text{cm}^{-1}$) and spin-orbit coupling H_{SO} ($10^3\,\text{cm}^{-1}$), i. e., $H_{ee} > H_{SO}$. To determine the free ion ground state use the following scheme and apply HUND's rules:

Ln^{3+}	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
N	1	2	3	4	5	6	7	8	9	10	11	12	13	14
m_s	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
m_l	$+3$	$+2$	$+1$	0	-1	-2	-3	$+3$	$+2$	$+1$	0	-1	-2	-3

1. The term with maximum S (or multiplicity $2S+1$) lies lowest in energy ($\sum_i m_{s,i} = M_S \rightarrow S$).
2. For a given multiplicity, the term with the highest value of L lies lowest in energy ($\sum_i m_{l,i} = M_L \rightarrow L$).
3. For atoms with less than half-filled shells, the level with the lowest value of J lies lowest ($J = |L - S|$), while the opposite rule applies (highest J lies lowest) when a subshell is more than half full ($J = L + S$).

Examples:
Pr^{3+} [$4f^2$]: $S = 1$, $L = 5$, $J = 4$; $g_J = \frac{4}{5}$, $\mu = 3.58\,\mu_B$ ($^3H_4$).
Dy^{3+} [$4f^9$]: $S = 5/2$, $L = 5$, $J = 15/2$; $g_J = \frac{4}{3}$, $\mu = 10.65\,\mu_B$ ($^6H_{15/2}$).

Table 2: Lanthanide ions: term symbol (ground state), one-electron spin-orbit coupling parameter ζ_{4f} [cm^{-1}], g_J, $g_J J$, $g_J[J(J+1)]^{1/2}$ and μ_{eff}^{exp}(295 K)

Ln^{3+}	$4f^N$	$^{2S+1}L_J$	ζ_{4f} [a]	g_J	$g_J J$	$g_J[J(J+1)]^{1/2}$	μ_{eff}^{exp}
La^{3+} [b]	$4f^0$	$^1S_0$				0	
Ce^{3+}	$4f^1$	$^2F_{5/2}$	625	6/7	15/7	2.535	2.3–2.5
Pr^{3+}	$4f^2$	$^3H_4$	758	4/5	16/5	3.578	3.4–3.6
Nd^{3+}	$4f^3$	$^4I_{9/2}$	884	8/11	36/11	3.618	3.4–3.5
Pm^{3+}	$4f^4$	$^5I_4$	1000	3/5	12/5	2.683	2.9 [c]
Sm^{3+}	$4f^5$	$^6H_{5/2}$	1157	2/7	5/7	0.845	1.6
Eu^{3+}	$4f^6$	$^7F_0$	1326	0	0	0	3.5
Gd^{3+}	$4f^7$	$^8S_{7/2}$	1450	2	7	7.937	7.8–7.9
Tb^{3+}	$4f^8$	$^7F_6$	1709	3/2	9	9.721	9.7–9.8
Dy^{3+}	$4f^9$	$^6H_{15/2}$	1932	4/3	10	10.646	10.2–10.6
Ho^{3+}	$4f^{10}$	$^5I_8$	2141	5/4	10	10.607	10.3–10.5
Er^{3+}	$4f^{11}$	$^4I_{15/2}$	2369	6/5	9	9.581	9.4–9.5
Tm^{3+}	$4f^{12}$	$^3H_6$	2628	7/6	7	7.561	7.5
Yb^{3+}	$4f^{13}$	$^2F_{7/2}$	2870	8/7	4	4.536	4.5
Lu^{3+} [b]	$4f^{14}$	$^1S_0$				0	

[a] The relation between ζ_{4f} and λ_{LS} of the Russell-Saunders ground term is given by $\lambda_{LS} = \pm(\zeta_{4f}/2S)$, where (+) and (−) sign correspond to $N \leq 2l+1$ and $N \geq 2l+1$ respectively.
[b] diamagnetic
[c] observed for Nd^{2+} compounds.

3.3 Lanthanide ions in octahedral ligand fields [5]

The chemical environment of the Ln ions has only a minor effect on the 4f electrons. The ligand field effect produces splittings of $H_{LF} \approx 10^2\,\mathrm{cm}^{-1}$ leading generally to temperature dependent μ and described by the effective

BOHR magneton number μ_{eff}:

$$\chi_{mol} = \mu_0 \frac{N_A \mu_{eff}^2 \mu_B^2}{3k_B T} \quad \text{where} \quad \mu_{eff} = \left(\frac{3k_B T \chi_{mol}}{\mu_0 N_A \mu_B^2} \right)^{1/2} = 797.7 (T\chi_{mol})^{1/2} \quad (8)$$

As a rule, μ_{eff} approaches the free Ln ion value for T above 200 K (see Table 2, Figures 3 – 7).

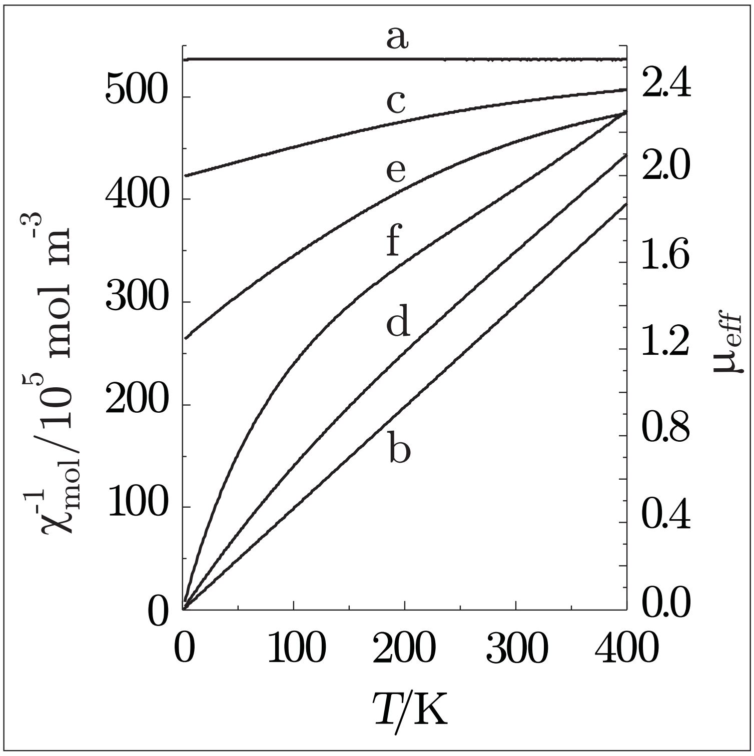


Fig. 3: Ce^{3+} in cubic ligand fields; χ_{mol}^{-1}–T- (b,d,f) and μ_{eff}–T diagrams (a,c,e); $\Delta = 605\,\mathrm{cm}^{-1}$ (e,f; oct.), $\Delta = -605\,\mathrm{cm}^{-1}$ (c,d; tet); straight lines (a,b) refer to the free ion.

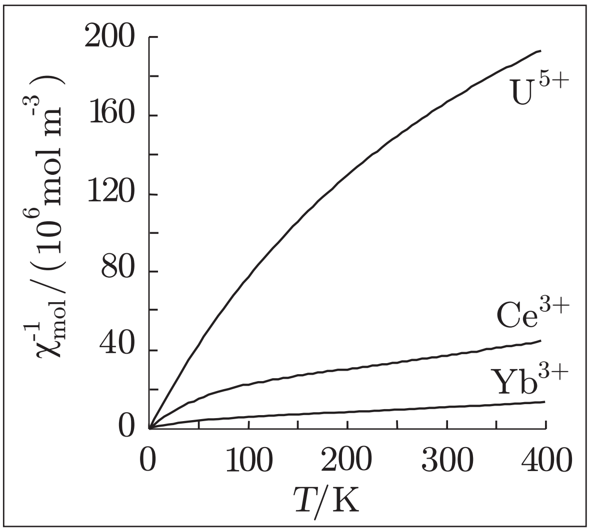


Fig. 4: Variation χ_{mol}^{-1} *vs.* T of Ce^{3+}, Yb^{3+}, and U^{5+} in octahedral coordination.

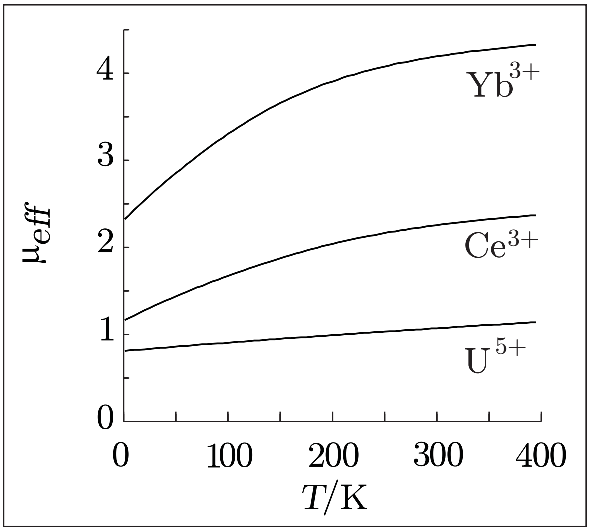


Fig. 5: Variation μ_{eff} *vs.* T of Ce^{3+}, Yb^{3+}, and U^{5+} in octahedral coordination.

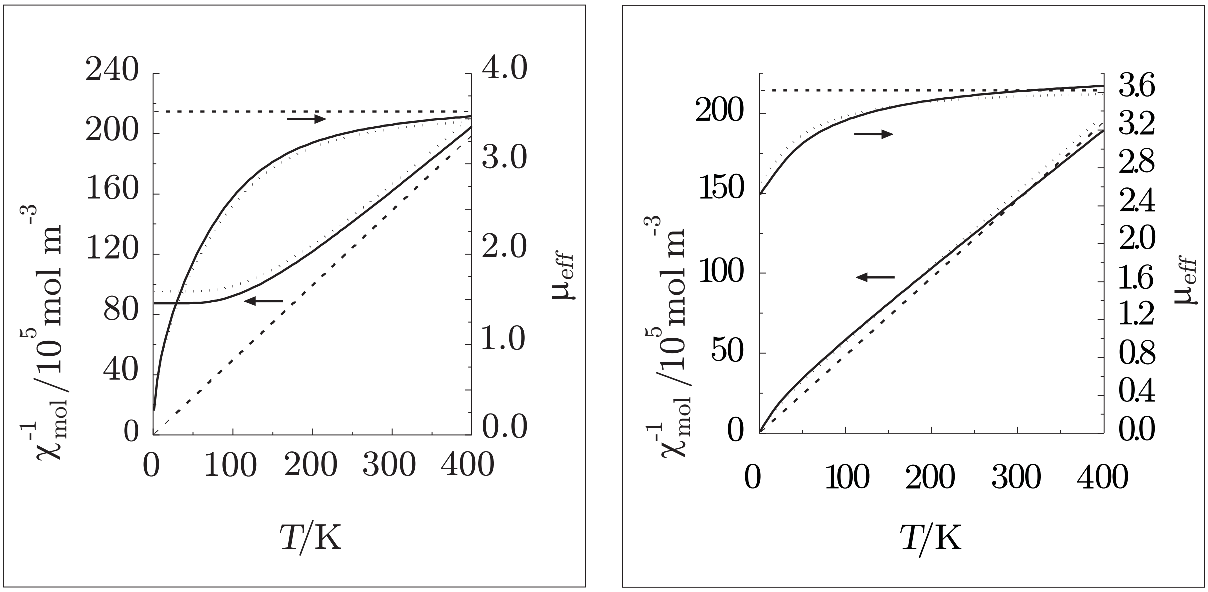


Fig. 6: χ_{mol}^{-1}–T and μ_{eff}–T diagrams for Pr^{3+} (left) and Nd^{3+} (right), calculated with the spectroscopically determined data of $Cs_2NaPrCl_6$ and $Cs_2NaNdCl_6$, respectively (solid lines: full basis; dottet lines: ground multiplet; dashed lines: free ions)

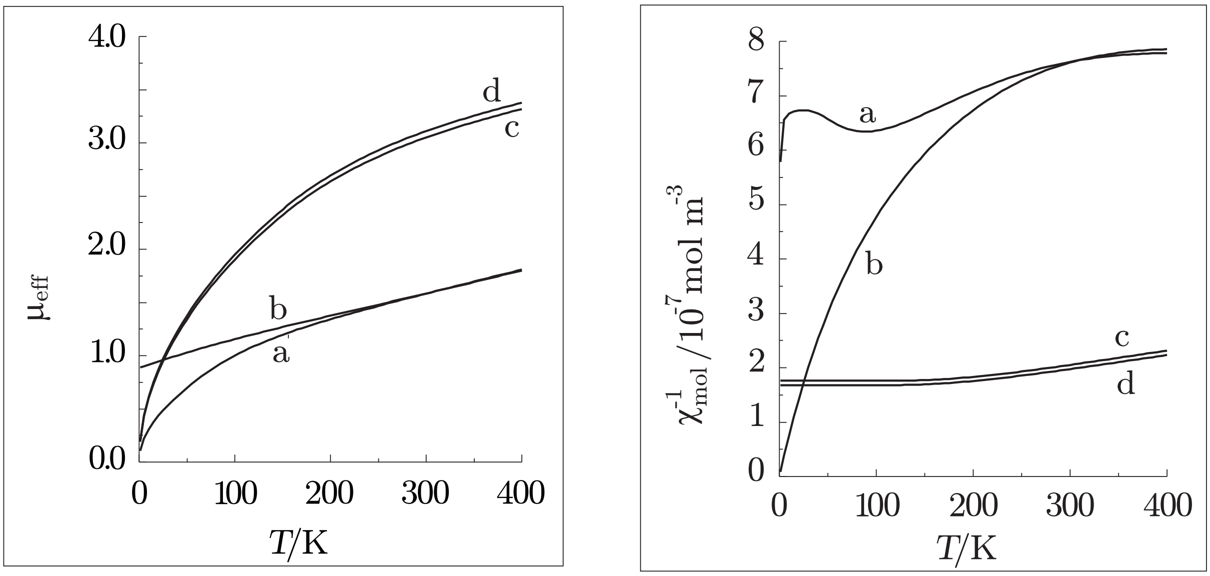


Fig. 7: μ_{eff}–T (left) and χ_{mol}^{-1}–T diagrams (right) for Sm^{3+} and Eu^{3+}, calculated with the spectroscopically determined data of $Cs_2NaYCl_6 : Sm^{3+}$ (a) and $Cs_2NaEuCl_6$ (d), respectively; free Sm^{3+} ion (b), free Eu^{3+} ion (c).

3.4 3d ions in octahedral ligand fields [4, 8, 6]

Tab. 3: Overview on the estimated magnetic behaviour of 3d systems (octahedral ligand field)

system	energetic order	N^a	ground state	$\chi_{mol}(T)$ ^{b}
$3d^N$	$H_{ee} \approx H_{LF} > H_{SO}$	5(hs)	$^6A_1$	$\chi_{mol} = C/T$
		1, 2, 6(hs), 7(hs)	T	$\chi_{mol} = f(T)$
		4(hs), 9	E	$\chi_{mol} = C'/T + \chi_0$
		3, 8	A_2	$\chi_{mol} = C'/T + \chi_0$
	$H_{LF} > H_{ee} > H_{SO}$	6(ls)	$^1A_1$	$\chi_{mol} = \chi_0$

[a]hs and ls assign high-spin and low-spin configuration, respectively.

[b]$\chi_{mol} = f(T)$ stands for complicated variation χ_{mol} *vs.* T (see Figure 8); C is the Curie constant, C' is a constant which deviates more or less from C caused by H_{LF} and H_{SO}, and χ_0 is a temperature independent parameter.

Tab. 4: Ions with $3d^N$ high-spin configuration: term symbols (ground state), one-electron spin-orbit coupling parameter ζ_{3d} [cm^{-1}] [4], S, $2\,[S(S+1)]^{1/2}$ and μ_{eff}^{exp} (295 K).

Ion	$3d^N$	$^{2S+1}L_J$	ζ_{3d}	S	$2[S(S+1)]^{1/2}$	μ_{eff}^{exp}
Ti^{3+}	$3d^1$	$^2D_{3/2}$	154	1/2	1.73	1.65 – 1.79
V^{3+}	$3d^2$	$^3F_2$	209	1	2,83	2.75 – 2.85
V^{2+}	$3d^3$	$^4F_{3/2}$	167	3/2	3.87	3.80 – 3.90
Cr^{3+}	$3d^3$	$^4F_{3/2}$	273	3/2	3.87	3.70 – 3.90
Cr^{2+}	$3d^4$	$^5D_0$	230	2	4.90	4.75 – 4.90
Mn^{3+}	$3d^4$	$^5D_0$	352	2	4.90	4.90 – 5.00
Mn^{2+}	$3d^5$	$^6S_{5/2}$	347	5/2	5.92	5.65 – 6.10
Fe^{3+}	$3d^5$	$^6S_{5/2}$	(460)	5/2	5.92	5.70 – 6.00
Fe^{2+}	$3d^6$	$^5D_4$	410	2	4.90	5.10 – 5.70
Co^{3+}	$3d^6$	$^5D_4$	(580)	2	4.90	5.30
Co^{2+}	$3d^7$	$^4F_{9/2}$	533	3/2	3.87	4.30 – 5.20
Ni^{3+}	$3d^7$	$^4F_{9/2}$	(715)	3/2	3.87	
Ni^{2+}	$3d^8$	$^3F_4$	649	1	2.83	2.80 – 3.50
Cu^{2+}	$3d^9$	$^2D_{5/2}$	829	1/2	1.73	1.70 – 2.20

Tab. 5: Ions with $3d^N$ low-spin configuration: no. of unpaired electrons N', S, $2\,[S(S+1)]^{1/2}$ and μ_{eff}^{exp} (295 K).

Ion	$3d^N$	structure	N'	S	$2[S(S+1)]^{1/2}$	μ_{eff}^{exp}
Cr^{2+}	$3d^4$	oct.(dist.)$^{a)}$	2	1	2.83	3.20 – 3.30
Mn^{3+}		oct.(dist.)				3.18
Mn^{2+}	$3d^5$	oct.(dist.)	1	1/2	1.73	1.80 – 2.10
Fe^{3+}		oct.(dist.)				2.0 – 2.5
Fe^{2+}	$3d^6$	oct.	0	0	0	0
Co^{3+}		oct.				TIP$^{b)}$
Co^{2+}	$3d^7$	oct.(dist.)	1	1/2	1.73	1.8
Ni^{2+}	$3d^8$	square planar	0	0	0	0

$^{a)}$ Distorted due to JAHN-TELLER effect.
$^{b)}$ Temperature independent paramagnetism.

$3d^1$: Example for temperature dependent μ_{eff}

$\mu_{eff} \sim \sqrt{T}$ for $T \leq 100\,\mathrm{K}$

$\chi_{mol}^{-1} \approx$ linear increase for $T \geq 150\,\mathrm{K}$

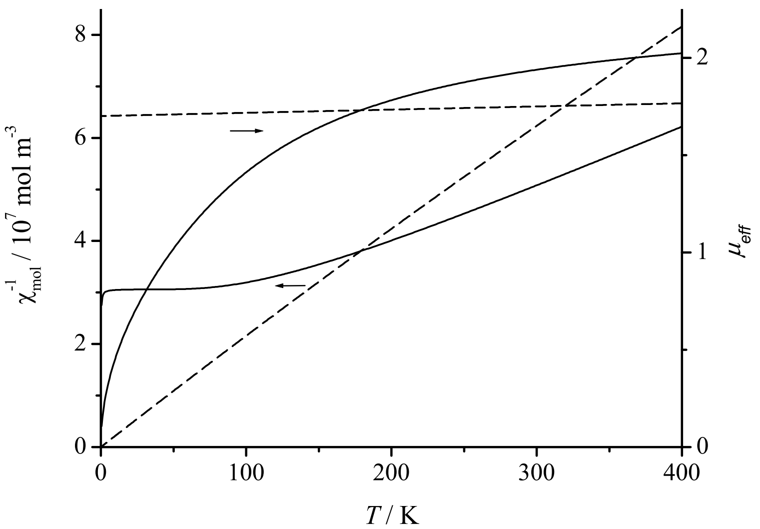


Fig. 8: Variation of μ_{eff} *vs.* T and χ_{mol}^{-1} *vs.* T plots of a $3d^1$ ion in octahedral (——) and orthorhombic (– – –) surrounding.

3.5 Curie-Weiss law

The Curie-Weiss law

$$\boxed{\chi_{mol} = \frac{C}{T - \Theta_p}} \qquad \text{with} \quad \Theta_p = \frac{2S(S+1)}{3k_B} \sum_i z_i \mathcal{J}_i \tag{9}$$

- is the most overworked formula in paramagnetism [7]
- has only a limited applicability:
  - not applicable to magnetic diluted systems
  - not applicable to systems like Ti^{3+} in octahedral surrounding (see Figure 8) and f systems (except Gd^{3+}, Eu^{2+})
  - only applicable to pure spin paramagnetism with C corresponding with the permanent magnetic moment μ and Θ_p measuring the total exchange interactions of a magnetically active centre with all its magnetic neighbours (nearest, next-nearest, etc.)

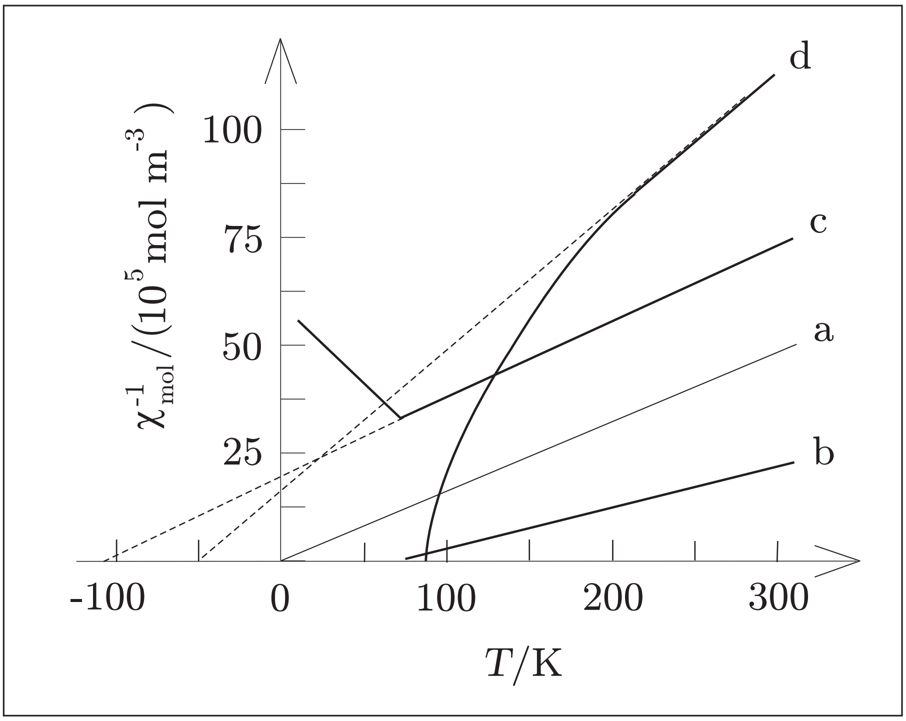
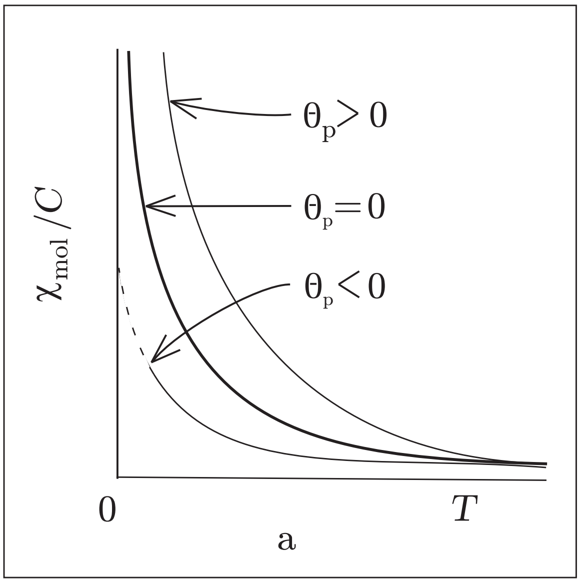
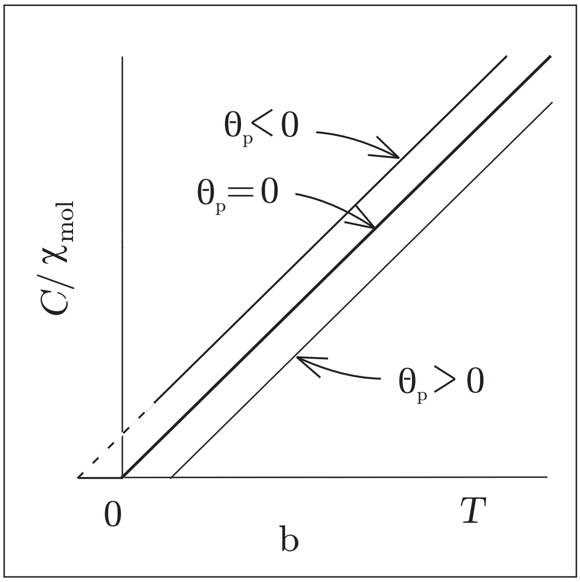
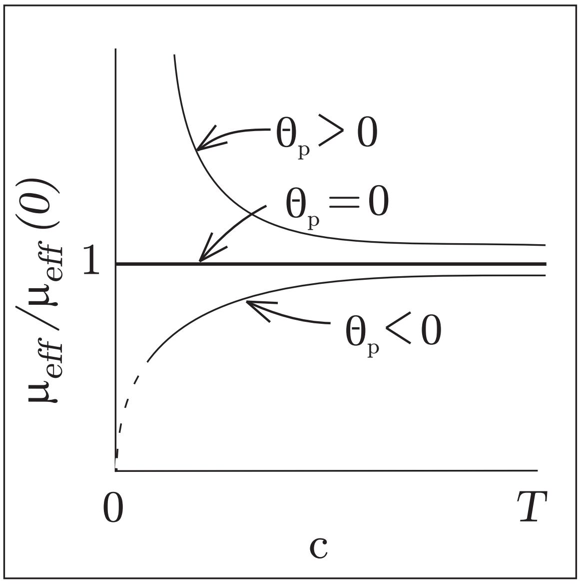


Fig. 9: χ^{-1} as a function of T for Curie law (**a**) and Curie-Weiss behaviour (schematic); (**b**): EuO, $\Theta_p = 74.2\,\text{K}$, $T_C = 69\,\text{K}$; (**c**): MnF_2, $\Theta_p = -113\,\text{K}$, $T_N = 74\,\text{K}$; (**d**): Na_2NiFeF_7, $\Theta_p = -50\,\text{K}$, $T_C = 88\,\text{K}$)





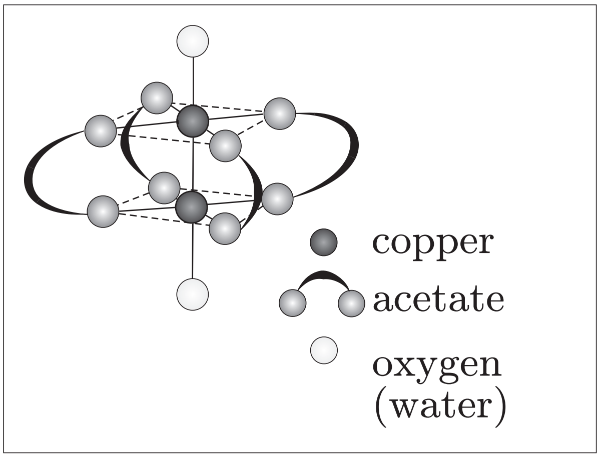


CURIE behaviour (bold lines) and CURIE-WEISS behaviour in reduced magnetic quantities χ_{mol}/C and $\mu_{eff}/\mu_{eff}(0)$ (C and $\mu_{eff}(0)$ refer to the free ion)

Fig. 10 a: variation χ_{mol} *vs.* T
Fig. 10 b: variation χ_{mol}^{-1} *vs.* T
Fig. 10 c: variation μ_{eff} *vs.* T

3.6 Exchange interactions in polynuclear compounds [9]

Example: Dinuclear complex $[Cu(CH_3COO)_2(H_2O)]_2$



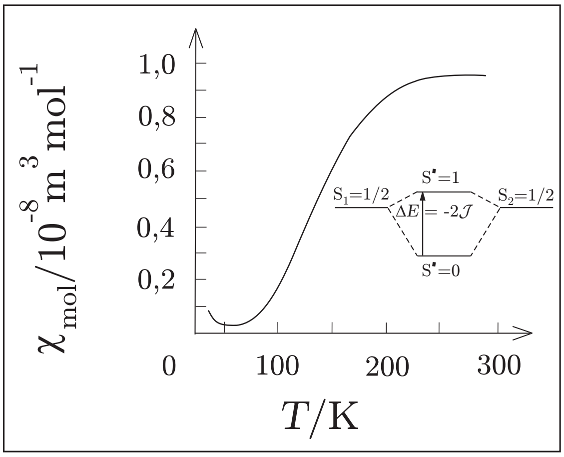


Fig. 11: $[Cu(CH_3COO)_2(H_2O)]_2$; left: molecular structure; right: χ_{mol} versus T diagram with $\mathcal{J} = -148\,\mathrm{cm}^{-1}$ ($\hat{H}_{ex} = -2\mathcal{J}\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2$), $g = 2.16$, $\chi_0 = 76 \times 10^{-11}\,\mathrm{m^3\,mol^{-1}}$. To explain $\mathcal{J} = -148\,\mathrm{cm}^{-1}$ both the direct exchange interactions between the $d_{x^2-y^2}$ orbitals and the superexchange *via* the doubly occupied orbitals as well as unoccupied orbitals of the bridging ligands have to be accounted for.

$$\chi_{mol} = \mu_0 \frac{N_A \mu_B^2 g^2}{3k_B T}\left[1 + \frac{1}{3}\exp\left(\frac{-2\mathcal{J}}{k_B T}\right)\right]^{-1} + \chi_0,$$ see section 6.3, page 54

Problems

1. How are the quantities (i) $\boldsymbol{m}$, (ii) μ_{eff}, (iii) μ, (iv) μ_m^s defined?

2. Calculate the spin contributions to the molar susceptibility of hydrogen atoms at 298 K (SI units).
   $\mu_0 N_A \mu_B^2/(3k_B) = 1.57141 \times 10^{-6}\mathrm{m^3\,K\,mol^{-1}}$

3. What are the electronic and structural conditions for a compound to be a paramagnet obeying the CURIE law? Give examples!

4. What are the electronic, structural, and thermal conditions for a compound to be a paramagnet obeying the CURIE-WEISS law $\chi_{mol} = C/(T - \Theta_p)$, permitting a reasonable interpretation C and Θ_p? Give examples!

5. Write the ground state term symbols ${}^{2S+1}L_J$ of free ions with electronic configuration [Ar] $3d^N$ ($N = 0, 1, 2, \ldots, 10$).

6. What levels (multiplets J) may arise from the terms (a) ${}^1S$, (b) ${}^2P$, (c) ${}^3P$, (d) ${}^3D$, (e) ${}^4D$? How many states (distinguished by the quantum number M_J) belong to each level?

4 Magnetic ordering

4.1 Ferromagnetism $\Uparrow\Uparrow\Uparrow\Uparrow$

4.1.1 Substances and materials

Table 6: Ferromagnetic elements and compounds

substance	structure	T_C/K	Θ_p/K	μ_m^s/μ_B
α-Fe	bcc	1044(2)	1100	2.216
β-Co	hcp	1388(2)	1415	1.715
Ni	ccp	627.4(3)	649	0.616
Gd	hcp	293.4	317	7.63
EuO	NaCl	69	74.2	6.94
$La_{1-x}Sr_xMnO_3$	perovskite	210−385		
$CrBr_3$	BiI_3	32.7	54	3.0

Tab. 7: Ferromagnetic materials: properties and application. T_C [K], μ_m^s [μ_B] per formula unit, $(BH)_{max}$ [kJ m^{-3}] (mr: magnetic data recording; sm: softmagnetic material; hm: hardmagnetic material)

material	structure	T_C	μ_m^s	$(BH)_{max}$ [a]	appl.
$Fe_{40}Co_{40}B_{20}$	amorphous	> 800	1.43		sm
supermalloy[b]	ccp	673			sm
Alnico[c]	[d]	> 800		25	hm
$SmCo_5$	$CaCu_5$	1000		160	hm
Sm_2Co_{17}	Th_2Zn_{17}			225	hm
$Nd_2Fe_{14}B$	$Nd_2Fe_{14}B$	585	37.6	360	hm
CrO_2	Rutil	392	2.00		mr

[a] $(BH)_{max}$ is the performance of a hardmagnetic material.
[b] Typical composition (mass %): Ni (79), Fe (15.5), Mo (5.0), Mn (0.5).
[c] Alnico 2 (mass %): Ni (18–21), Al (8–10), Co (17–20), Cu (2–4), Nb (0–1), Fe (rest).
[d] Heterogeneous system: ferromagnetic segregations (Fe/Co) in a (Ni/Al) matrix.

4.1.2 Hysteresis loop and magnetisation curve

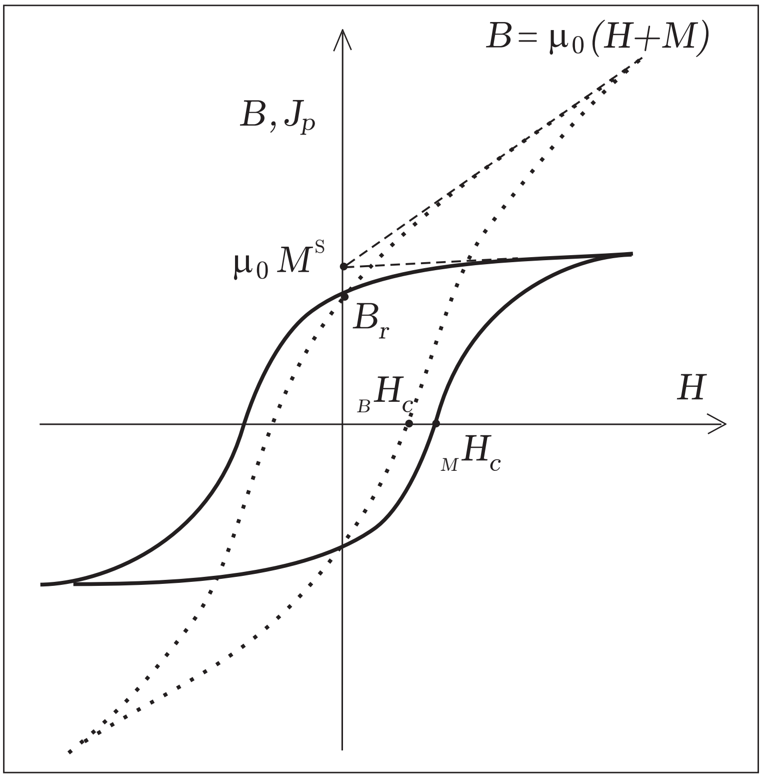


Fig. 12: Hysteresis loop of a ferromagnet; B as a function of H (—) and $\mu_0 M$ as a function of H ($\cdots$), $\mu_0 M = J_p$, J_p: magnetic polarisation)

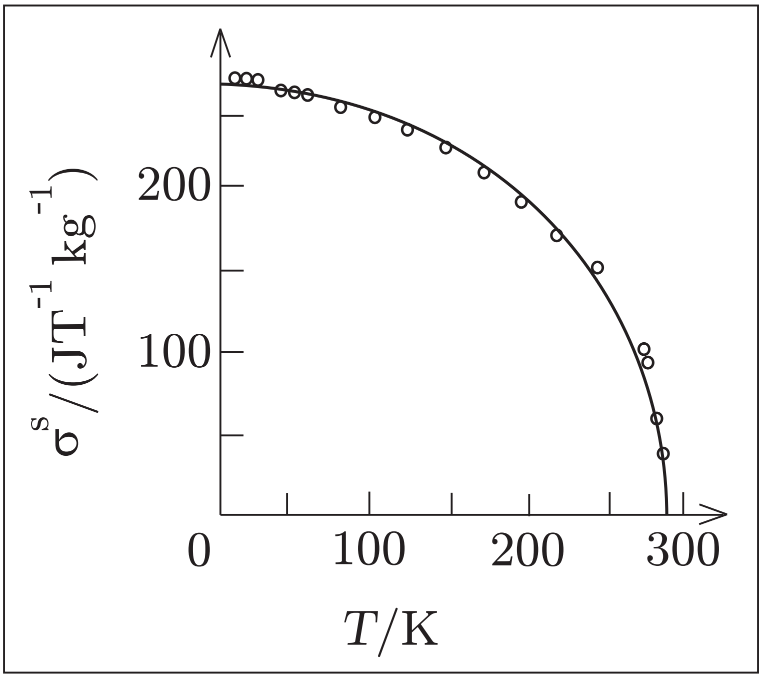


Fig. 13: σ^s as a function of T of gadolinium ($\sigma^s = M^s/\rho$)

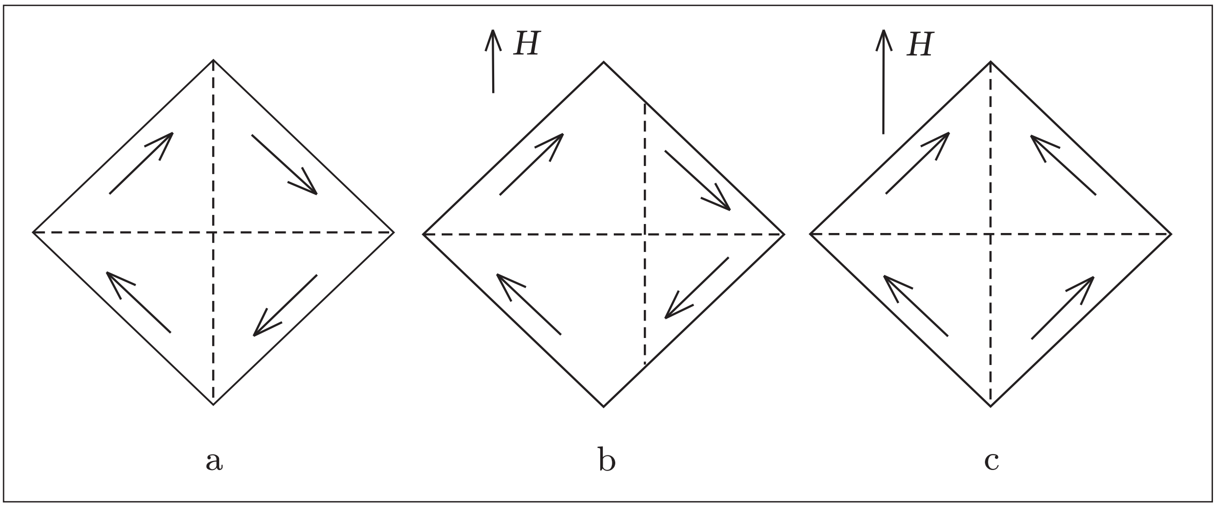


Fig. 14: Schematic representation of domains in a ferromagnetic monocrystal: (a) unmagnetised; (b) magnetisation through movement of domain boundary walls; domains oriented parallel to $\boldsymbol{H}$ grow at the expense of antiparallel domains; (c) magnetisation by rotation of the magnetisation vector of whole domains. The domains remain oriented along a preferred direction; stronger fields are required to swing the magnetisation vectors towards the applied field [2].

4.2 Antiferromagnetism $\Uparrow\Downarrow\Uparrow\Downarrow$

Tab. 8: Antiferromagnetic compounds

substance	structure	T_N/K	Θ_p/K	μ_m^s/μ_B
MnO	NaCl	118	−610	5.0
FeO	NaCl	185	−570	3.3
CoO	NaCl	292		3.8
NiO	NaCl	523		2.0
Co_3O_4	spinel	40		3.02
$ZnFe_2O_4$	spinel	10.6	0	4.0
MnF_2	rutile	74	−113	4.98

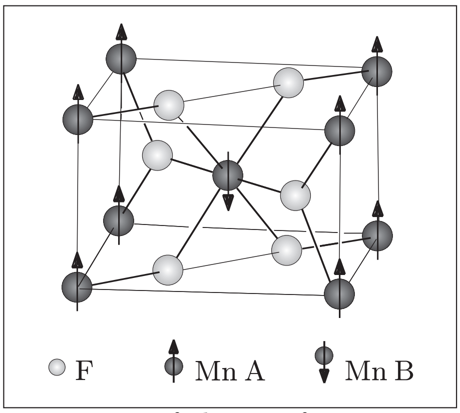


Fig. 15: Spin structure of the antiferromagnet MnF_2 (rutile type); A, B: Mn^{2+} sublattices

4.3 Ferrimagnetism ⇑↓⇑↓

4.3.1 Substances and materials

Tab. 9: Ferrimagnetic compounds and materials

substance/material	structure	T_C/K	Θ_p/K	μ_m^s/μ_B
Mn_3O_4	spinel	42		1.85
Fe_3O_4	spinel(inverse)	858		4.1
$NiFe_2O_4$	spinel(inverse)	858		2.3
Na_2NiFeF_7	weberite	88	-50	2.2 (Ni)
				5.0 (Fe)

4.3.2 Magnetic saturation moment

$\mu_m^s = M^s \mathrm{M}_r/(\rho N_A) = M_{mol}^s/N_A$

Arrangements of magnetic dipoles in ferrimagnets

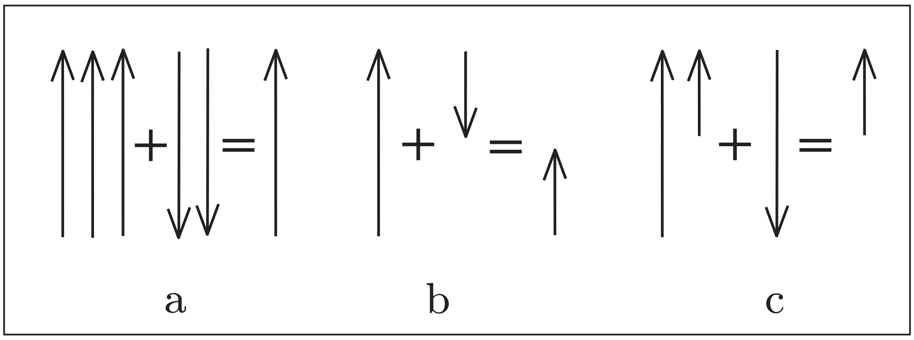


Fig. 16: Three possible arrangements of magnetic dipoles in ferrimagnetic materials: (a) unequal numbers of identical moments on the two sublattices; (b) unequal moments on the two sublattices; (c) two equal moments and one unequal [2].

Example $Fe_3O_4 \mathrel{\widehat{=}} Fe^{III}[Fe^{II}Fe^{III}]O_4$ **(inverse spinel)**:

$\mu_m^s = gS\mu_B$ with $g = 2$ (pure spin magnetism) of the iron ions occupying tetrahedral (A) and octahedral holes (B):

$Fe^{3+}(A)$: $\mu_m^s = 5\,\mu_B$
$Fe^{3+}(B)$: $\mu_m^s = 5\,\mu_B$
$Fe^{2+}(B)$: $\mu_m^s = 4\,\mu_B$

Resultant moment $\mu_m^s(\mathrm{Fe_3O_4})$:

$\mu_m^s(B) - \mu_m^s(A) = (5+4)\,\mu_B - 5\,\mu_B = 4\,\mu_B$ per formula unit

(exp.: $4.1\,\mu_B$)

NÉEL's suggestion: all interactions in the ferrites are antiferromagnetic, but the A–B interaction is considerably stronger than A–A or B–B. Thus, in the inverse spinel structure the dominating A–B interaction makes the spins within each sublattice parallel, despite their mutual antiferromagnetic interaction. This is supported by the fact, that $\mathrm{ZnFe_2O_4}$, which has the normal structure, has no net saturation moment.

Examples: Mixed ferrites made of $\mathrm{M^{II}[Fe^{III}]O_4}$ **and** $\mathrm{Fe^{III}[M^{II}Fe^{III}]O_4}$**:**

Mixing two ferrites, three cases can be distinguished: 1.) Both ferrites are inverse, 2.) one is normal, the other inverse, 3.) both are normal. While 3.) is practically of no relevance, 1.) and 2.) are of interest.

1. Both base ferrites inverse
   $\mathrm{M_i^{II}}$ (amount x, $\mu_m^s(\mathrm{M_i})$) and $\mathrm{M_j^{II}}$ (amount $1-x$, $\mu_m^s(\mathrm{M_j})$) on site B:

   $$\mu_m^s = x\,\mu_m^s(\mathrm{M_i}) + (1-x)\,\mu_m^s(\mathrm{M_j})$$

   Example: $\mathrm{Fe[Ni_xMn_{1-x}Fe]O_4}$:
   $\mathrm{Fe[NiFe]O_4}$: $\mu_m^s \approx 2.3\,\mu_B$, $T_C \approx 900\,\mathrm{K}$
   $\mathrm{Fe[MnFe]O_4}$: $\mu_m^s \approx 4.7\,\mu_B$, $T_C \approx 580\,\mathrm{K}$
   linear variation μ_m^s *vs.* x (and also T_C *vs.* x)

2. Normal and inverse base ferrite
   Provided $\mathrm{M_i^{II}}$ is diamagnetic ($\mu_m^s(\mathrm{M_i}) = 0$), $\mathrm{M_i^{II}[Fe_2^{III}]O_4}$. Substituting $\mathrm{M_j^{II}}$ in $\mathrm{Fe^{III}[M_j^{II}Fe^{III}]O_4}$ by $\mathrm{M_i^{II}}$, the latter occupies site A. In return for it, $\mathrm{Fe^{III}}$ changes from A to B. The net moment of the mixed ferrite amounts to

   $$\mu_m^s = (1-x)\,\mu_m^s(\mathrm{M_j}) + 2x\,\mu_m^s(\mathrm{Fe^{III}})$$

   Since always $\mu_m^s(\mathrm{M_j}) < \mu_m^s(\mathrm{Fe^{III}})$, the net moment increases with further incorporation of $\mathrm{M_i^{II}}$. For $x = 1$, however, μ_m^s must be zero, because $\mathrm{M_iFe_2O_4}$ is a normal ferrite, which is antiferromagnetic. Thus, μ_m^s passes through a maximum, reflecting the increasing antiferromagnetic coupling B–B and the decreasing A–B interaction according to the increasing $\mathrm{M_i}$ amount.

4.3.3 Paramagnetism above the CURIE temperature T_C [5]

In the ferrite MFe_2O_4 the M^{II} ions are considered as diamagnetic and the magnetically active Fe^{3+} ions are distributed over the A and B sites. $M^s_{mol,A}$ and $M^s_{mol,B}$ assign the magnetisation per mole of the Fe^{3+} ions, if they occupy the A and B sites, respectively. In general, $M^s_{mol,A}$ and $M^s_{mol,B}$ differ on account of the different ligand field effects acting on the iron ions. The net magnetisation ($T < T_C$) of the ferrite is

$$\boldsymbol{M}^s_{mol} = x\boldsymbol{M}^s_{mol,A} + y\boldsymbol{M}^s_{mol,B} \quad \text{with} \quad x + y = 1, \tag{10}$$

where x and y give the amount of Fe^{3+} ions on A and B sites, respectively. For $T > T_C$, molecular field theory leads to (see ref. [5]):

$$\begin{aligned} \frac{1}{\chi_{mol}} &= \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T-\Theta} \quad \text{with} \\ \chi_0^{-1} &= n(2xy - x^2\alpha - y^2\beta), \\ \sigma &= n^2Cxy\left[x(1+\alpha) - y(1+\beta)\right]^2, \\ \Theta &= nCxy[2+\alpha+\beta]. \end{aligned} \tag{11}$$

The positive molecular field parameter n stands for the strength of the antiferromagnetic interaction *between* the sublattices A and B, whereas $n\alpha$ and $n\beta$ refer to the interaction *in* the sublattices A and B, respectively. The variation χ^{-1}_{mol} *vs.* T (Gl. (11)) is not linear in contrast to the CURIE-WEISS law. Instead, a hyperbola with asymptotes

$$\chi^{-1}_{mol} = T/C + \chi_0^{-1} \tag{12}$$

and

$$T = \Theta \tag{13}$$

is obtained (see Figure 17).

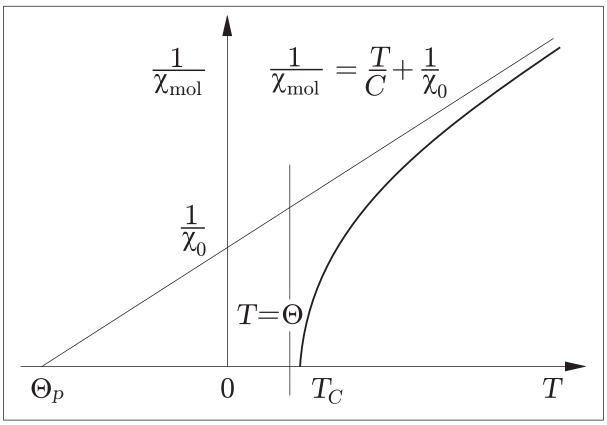


Fig. 17: χ^{-1}_{mol} *vs.* T of a simple ferrimagnet

Remarks to eq. (11):

- The characteristic feature of a ferrimagnetic material is the hyperbolic variation χ_{mol}^{-1} *vs.* T (in contrast to ferromagnetic materials where the molecular field approximation gives a straight line).

- A linear dependence is obtained for $\sigma = 0$ and $x(1+\alpha) = y(1+\beta)$, fulfilled for $x = y = 1/2$ and $\alpha = \beta$, which corresponds to antiferromagnetism.

- The intersection of the asymptote eq. (12) with the T axis at $\Theta_p = -C/\chi_0$ is called asymptotic CURIE point. It corresponds with the paramagnetic CURIE temperature of an antiferromagnet in the case of $x = y = 1/2$ and $\alpha = \beta$.

- The intersection of the hyperbola eq. (11) with the T axis is of great importance:

  $$T_C = \frac{nC}{2}\left\{x\alpha + y\beta + [(x\alpha - y\beta)^2 + 4xy]^{1/2}\right\}$$

  $T_C > 0$ means, that at $T = T_C$ the susceptibility diverges ($\chi \to \infty$), i. e., for $T < T_C$ spontaneous magnetisation exists. In the case of $T_C < 0$, the substance behaves paramagnetically in the whole temperature range.

- When $\alpha > 0$ and $\beta > 0$ ferrimagnetism exists. If the absolute values of α and β exceed those values, which fulfill the condition $\alpha\beta = 1$, the moment ordering on the sublattices is antiferromagnetic or nonmagnetic. If the absolute values are smaller than the values which fulfill $\alpha\beta = 1$, the antiferromagnetic interactions within the sublattices are quenched, so that spontaneous magnetisation results.

Problems

1. What is a hard magnetic material? Give examples!
2. Fe_3O_4 adopts the inverse spinel structure type. What type of magnetic structure is expected? How large is the magnetic saturation moment per formula unit so long as pure spin magnetism is assumed?
3. Co_3O_4 is a spinel with an antiferromagnetic magnetic structure at $T < 40\,\mathrm{K}$. Neutron diffraction yields the magnetic saturation moment $\mu_m^s = 3\,\mu_B$ for the magnetically active centres. What are the magnetically active centres? Is the spinel normal or inverse? What are the spin configurations and total spin quantum numbers of the centres?
4. $NiFe_2O_4$ is an inverse spinel. What type of magnetic ordering is expected? How large is the magnetic saturation moment of each centre, so long as pure spin contributions are considered? What is the μ_m^s value per formula unit determined, e. g., by SQUID magnetometry?
5. EuO (NaCl type) is paramagnetic at $T > 70\,\mathrm{K}$ and obeying the Curie-Weiss law. How large is the expected paramagnetic moment μ, deduced from the slope of the Curie-Weiss straight line? What type of magnetic structure exists at $T < 70\,\mathrm{K}$, if neutron diffraction yields only an increase of reflection intensities, but no extra lines compared to those at $T > 70\,\mathrm{K}$? Consequently, what sign is expected for Θ_p?
6. What law is expected to describe the temperature dependence of the magnetic susceptibility of magnetically concentrated Mn(II) high-spin compounds above the magnetic ordering temperature T_C (Curie temperature) and T_N (Néel temperature), respectively? What information can be gained from a corresponding measurement with regard to the magnetic centres and the existing interactions?

5 Theory of free ions

5.1 Foundations of quantum-mechanics ([10]9–12)

Postulate 1. The state of a system is fully described by the wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, t)$.
Postulate 2. Observables are represented by operators chosen to satisfy the commutation relation

$$\hat{q}\hat{p}_q - \hat{p}_q\hat{q} = [\hat{q}, \hat{p}_q] = i\hbar \qquad (q = x, y, z; \quad i = \sqrt{-1}) \tag{14}$$

Example 5.1 *Application of the commutation relation*

$$\hat{x} = x\cdot \quad \text{and} \quad \hat{p}_x = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}$$

$$\begin{aligned}
\hat{x}\hat{p}_x\Psi &= x\frac{\hbar}{i}\frac{\mathrm{d}\Psi}{\mathrm{d}x} \\
\hat{p}_x\hat{x}\Psi &= \frac{\hbar}{i}\frac{\mathrm{d}(x\Psi)}{\mathrm{d}x} = \frac{\hbar}{i}\left(\Psi + x\frac{\mathrm{d}\Psi}{\mathrm{d}x}\right) \\
(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\Psi &= -\frac{\hbar}{i}\Psi = i\hbar\Psi
\end{aligned}$$

5.2 Perturbation theory ([5]83–91)

1. *Non-degenerate states*

$$\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \qquad \text{unperturbed system} \tag{15}$$

Hamilton operator of the perturbed system:

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$$

Schrödinger equation of the perturbed system:

$$\hat{H}\Psi_n = E_n\Psi_n; \qquad \text{find} \quad E_n, \Psi_n \tag{16}$$

Series expansion of Ψ_n und E_n:

Tab. 10: Classical and quantum-mechanical forms of E_{kin} and E_{pot}

Quantity	D[a]	classical	quantum-mechanical
E_{kin}	1	$\frac{m_e v_x^2}{2} = \frac{p_x^2}{2m_e}$	$\frac{\hat{p}_x^2}{2m_e} = \frac{1}{2m_e}\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 = -\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$
	3	$\frac{p^2}{2m_e}$	$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m_e}\nabla^2$ [b]
E_{pot} [c]	1	$-eV(x)$	$-e\hat{V}(x) = -eV(x)\cdot$
	3	$-eV(\boldsymbol{r})$	$-e\hat{V}(\boldsymbol{r}) = -eV(\boldsymbol{r})\cdot$

[a] Dimension.
[b] ∇ is the Nabla operator.
[c] Valid for one electron with charge $-e$ in the potential V.

$$\Psi_n = \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \ldots \qquad (17)$$
$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots . \qquad (18)$$

Insert the series into eq. (16):

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \ldots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \ldots),$$

Ordering of the terms with regard to powers of λ:

$$\hat{H}^{(0)}\Psi_n^{(0)} + \lambda\big(\hat{H}^{(1)}\Psi_n^{(0)} + \hat{H}^{(0)}\Psi_n^{(1)}\big) + \lambda^2\big(\hat{H}^{(1)}\Psi_n^{(1)} + \hat{H}^{(0)}\Psi_n^{(2)}\big) + \ldots = E_n^{(0)}\Psi_n^{(0)} + \lambda\big(E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\Psi_n^{(1)}\big) + \lambda^2\big(E_n^{(2)}\Psi_n^{(0)} + E_n^{(1)}\Psi_n^{(1)} + E_n^{(0)}\Psi_n^{(2)}\big) + \ldots .$$

$$\begin{array}{lrcl}
\lambda^0 & \hat{H}^{(0)}\Psi_n^{(0)} & = & E_n^{(0)}\Psi_n^{(0)} \qquad (19)\\
\lambda^1 & (\hat{H}^{(0)} - E_n^{(0)})\Psi_n^{(1)} & = & (E_n^{(1)} - \hat{H}^{(1)})\Psi_n^{(0)} \qquad (20)\\
\lambda^2 & (\hat{H}^{(0)} - E_n^{(0)})\Psi_n^{(2)} & = & E_n^{(2)}\Psi_n^{(0)} + (E_n^{(1)} - \hat{H}^{(1)})\Psi_n^{(1)} \qquad (21)\\
\vdots & & \vdots &
\end{array}$$

The first-order correction to the energy $E_n^{(1)}$
(premultiply both sides of eq. (20) with $\Psi_n^{(0)*}$ and integrate)

$$\underbrace{\int \Psi_n^{(0)*}\hat{H}^{(0)}\Psi_n^{(1)}d\tau - E_n^{(0)}\int \Psi_n^{(0)*}\Psi_n^{(1)}d\tau}_{0} = E_n^{(1)} - \int \Psi_n^{(0)*}\hat{H}^{(1)}\Psi_n^{(0)}d\tau$$

$$\boxed{E_n^{(1)} = \langle n|\hat{H}^{(1)}|n\rangle} \qquad (22)$$

The first-order correction to the wavefunction:

$$\boxed{\Psi_n^{(1)} = -\sum_{m\neq n}\frac{\langle m|\hat{H}^{(1)}|n\rangle}{E_m^{(0)} - E_n^{(0)}}\,\Psi_m^{(0)}} \qquad (23)$$

The second-order correction to the energy:

$$\boxed{E_n^{(2)} = -\sum_{m\neq n}\frac{\left|\langle m|\hat{H}^{(1)}|n\rangle\right|^2}{E_m^{(0)} - E_n^{(0)}}} \qquad \text{(see Fig. 18)} \qquad (24)$$

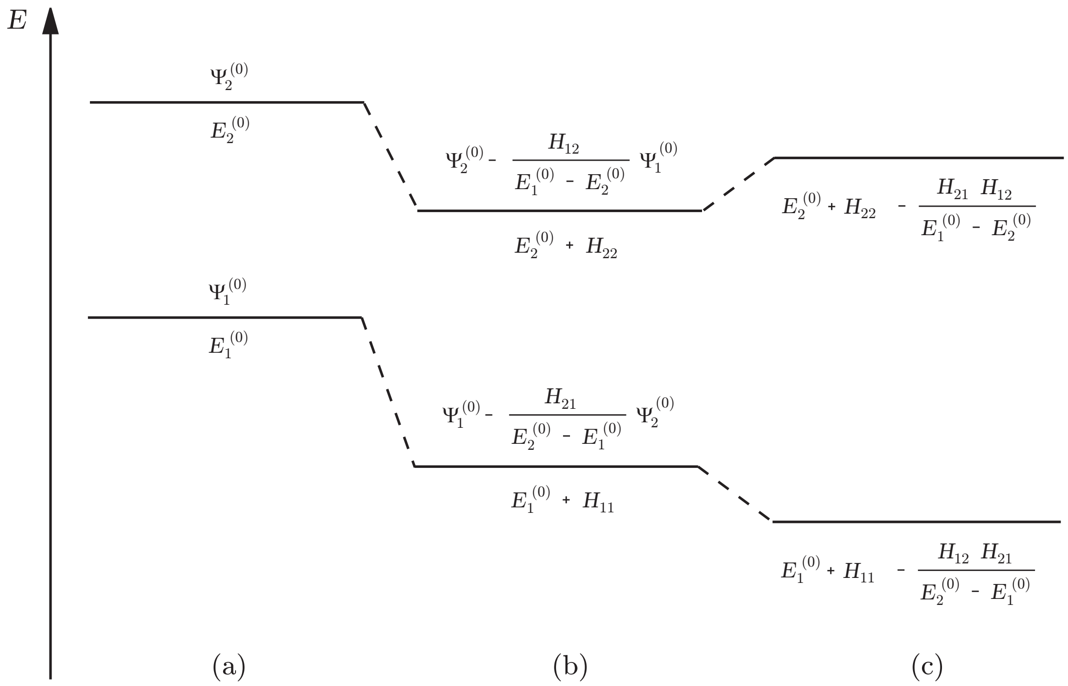


Fig. 18: Illustration of the possible effects of a perturbation on two non-degenerate levels; (a) 0^{th},(b) 1^{st},(c) 2^{nd} order

2. *Degenerate states*

Eq. (22) – (24) apply also in this case; in addition, the correct zeroth-order wavefunctions have to be determined (see Fig. 19):

Example: doubly degenerate pair of states

$$\hat{H}^{(0)}\Psi^{(0)}_{n,i} = E^{(0)}_n\Psi^{(0)}_{n,i} \qquad (i = 1, 2) \tag{25}$$

$$\Psi^{(0)}_n = u_1\Psi^{(0)}_{n,1} + u_2\Psi^{(0)}_{n,2} \tag{26}$$

The 'correct' linear combinations are those which correspond to the perturbed functions for $\lambda \to 0$.

Determination of u_1 and u_2:

Substituting eq. (26) in eq. (17); eq. (20) now reads:

$$\big(\hat{H}^{(0)} - E^{(0)}_n\big)\Psi^{(1)}_n = \big(E^{(1)}_n - \hat{H}^{(1)}\big)\big(u_1\Psi^{(0)}_{n,1} + u_2\Psi^{(0)}_{n,2}\big) \tag{27}$$

Multiply with $\Psi^{(0)*}_{n,1}$ and $\Psi^{(0)*}_{n,2}$, respectively and integrate:

$$\begin{aligned} u_1\big(H_{11} - E^{(1)}_n\big) + u_2H_{12} &= 0 \\ u_1H_{21} + u_2\big(H_{22} - E^{(1)}_n\big) &= 0 \end{aligned} \qquad \text{where} \quad H_{ij} = \int \Psi^{(0)*}_{n,i}\,\hat{H}^{(1)}\,\Psi^{(0)}_{n,j}\,d\tau$$

Under the condition that the determinant of the coefficients of u_1 and u_2 disappears the non-trivial solutions of this pair of equations are obtained:

$$\begin{vmatrix} H_{11} - E^{(1)}_n & H_{12} \\ H_{21} & H_{22} - E^{(1)}_n \end{vmatrix} = 0 \tag{28}$$

$$E^{(1)}_{n(1,2)} = \big(H_{11} + H_{22}\big)/2 \pm \sqrt{(H_{11} - H_{22})^2/4 + |H_{12}|^2}$$

$$u_{1(1,2)}(H_{11} - E^{(1)}_{n(1,2)}) + u_{2(1,2)}H_{12} = 0; \qquad x_{(1,2)} = \frac{u_{1(1,2)}}{u_{2(1,2)}} = -\frac{H_{12}}{H_{11} - E^{(1)}_{n(1,2)}}$$

Normalisation:

$$x^2_{(1,2)}u^2_{2(1,2)} + u^2_{2(1,2)} = 1 \quad \Rightarrow \quad \begin{cases} u_{2(1,2)} = \dfrac{1}{\sqrt{x^2_{(1,2)} + 1}} \\ u_{1(1,2)} = x_{(1,2)}u_{2(1,2)} = \dfrac{x_{(1,2)}}{\sqrt{x^2_{(1,2)} + 1}} \end{cases}$$

Correct zeroth-order wavefunction for the energy $E^{(1)}_{n(1,2)}$:

$$\Psi^{(0)}_{n(1,2)} = u_{1(1,2)}\Psi^{(0)}_{n,1} + u_{2(1,2)}\Psi^{(0)}_{n,2}$$

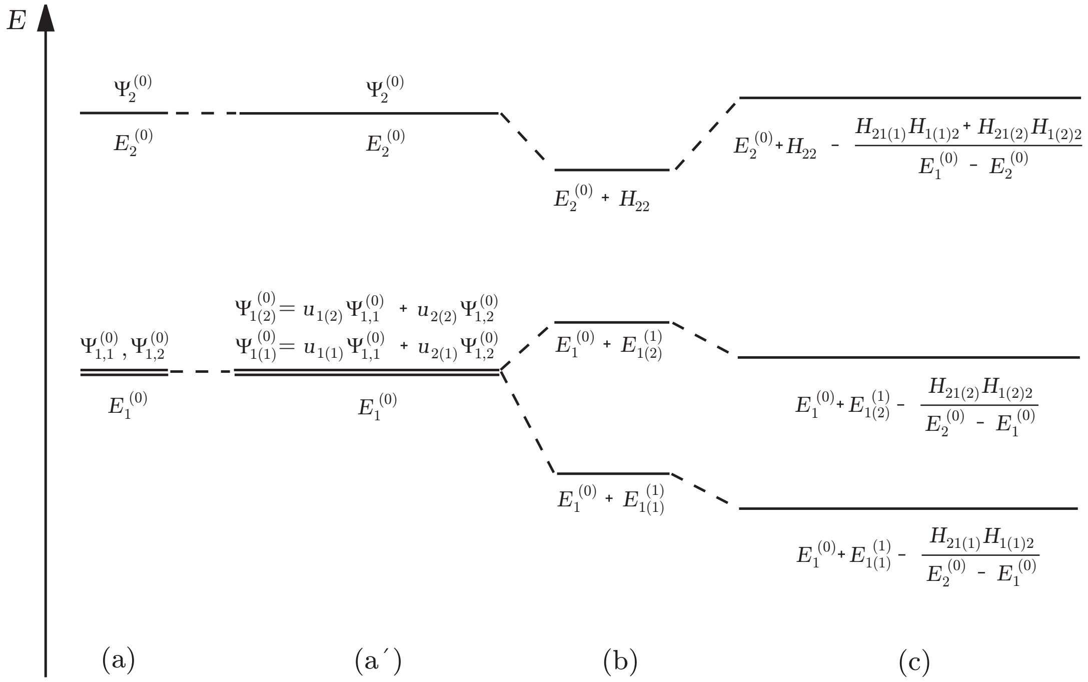


Fig. 19: Illustration of the possible effects of a perturbation on a doubly degenerate ground state and a non-degenerate excited state; (a) 0^{th}, (a') correct 0^{th}, (b) 1^{st},(c) 2^{nd} order

5.3 One-electron systems ([5]91–96)

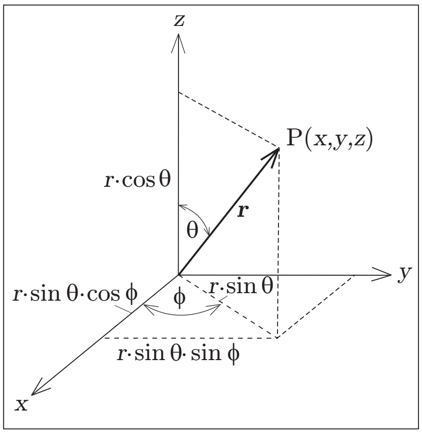
SCHRÖDINGER equation (spin ignored):

$$\Big[-\frac{\hbar^2}{2m_e}\nabla^2 - e\hat{V}(r)\Big]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{29}$$

For convenience the eigenfunctions (atomic orbitals) are given in spherical polar coordinates:

$$\psi(\boldsymbol{r}) = \psi_{n,l,m_l}(r,\theta,\phi) = \underbrace{R_{n,l}(r)}_{\text{radial f.}}\,\underbrace{Y^l_{m_l}(\theta,\phi)}_{\text{angular f.}} = R_{n,l}(r)\,\Theta^l_{m_l}(\theta)\,\sqrt{\frac{1}{2\pi}}\,e^{im_l\phi}$$

The functions $Y^l_{m_l}(\theta,\phi)$ are the (in general, complex) spherical harmonics specified by the quantum numbers l and m_l (see Table 11). They play a predominant role in magnetism.



$$
\begin{aligned}
x &= r \cdot \sin\theta \cdot \cos\phi \\
y &= r \cdot \sin\theta \cdot \sin\phi \\
z &= r \cdot \cos\theta
\end{aligned} \tag{30}
$$

$$
\begin{aligned}
r^2 &= x^2 + y^2 + z^2 \\
\cos\theta &= z/r \\
\tan\phi &= y/x
\end{aligned} \tag{31}
$$

Fig. 20: Relation between cartesian coordinates and spherical polar coordinates

Real functions (see Table 12) are gained by linear combinations

$$
\begin{aligned}
\tfrac{1}{\sqrt{2}}\left[-\psi_{n,l,m_l} + \psi_{n,l,-m_l}\right] &= \tfrac{1}{\sqrt{\pi}} R_{n,l}(r)\Theta^l_{-m_l}(\theta)\,\cos m_l\phi \\
\tfrac{1}{i\sqrt{2}}\left[-\psi_{n,l,m_l} - \psi_{n,l,-m_l}\right] &= \tfrac{1}{\sqrt{\pi}} R_{n,l}(r)\Theta^l_{-m_l}(\theta)\,\sin m_l\phi
\end{aligned} \tag{32}
$$

$$
\begin{aligned}
\tfrac{1}{\sqrt{2}}\left[\psi_{n,l,m_l} + \psi_{n,l,-m_l}\right] &= \tfrac{1}{\sqrt{\pi}} R_{n,l}(r)\Theta^l_{m_l}(\theta)\,\cos m_l\phi \\
\tfrac{1}{i\sqrt{2}}\left[\psi_{n,l,m_l} - \psi_{n,l,-m_l}\right] &= \tfrac{1}{\sqrt{\pi}} R_{n,l}(r)\Theta^l_{m_l}(\theta)\,\sin m_l\phi.
\end{aligned} \tag{33}
$$

For completely describing the wave function, the spin has to be taken into consideration. If spin-orbit coupling is ignored, the total function (*spin orbital*) is

$$
\psi(r,\theta,\phi;\sigma) = \psi(r,\theta,\phi)\,\psi(\sigma) \quad \text{where} \quad \sigma = \pm\frac{1}{2}. \tag{34}
$$

Table 11: Spherical harmonics for $l = 0, 1, 2, 3$

l	m_l	$Y^l_{m_l}(\theta, \phi)$ [a)]	$Y^l_{m_l}(x, y, z)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$\left(\frac{3}{4\pi}\right)^{1/2} \frac{z}{r}$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi}$	$\mp\left(\frac{3}{8\pi}\right)^{1/2} \frac{x \pm iy}{r}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$\left(\frac{5}{16\pi}\right)^{1/2} \frac{3z^2 - r^2}{r^2}$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta \sin\theta\, e^{\pm i\phi}$	$\mp\left(\frac{15}{8\pi}\right)^{1/2} \frac{z(x \pm iy)}{r^2}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{\pm i2\phi}$	$\left(\frac{15}{32\pi}\right)^{1/2} \frac{(x \pm iy)^2}{r^2}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$	$\left(\frac{7}{16\pi}\right)^{1/2} \frac{z(5z^2 - 3r^2)}{r^3}$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta (5\cos^2\theta - 1) e^{\pm i\phi}$	$\mp\left(\frac{21}{64\pi}\right)^{1/2} (x \pm iy) \frac{(5z^2 - r^2)}{r^3}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2} \cos\theta \sin^2\theta\, e^{\pm i2\phi}$	$\left(\frac{105}{32\pi}\right)^{1/2} \frac{z(x \pm iy)^2}{r^3}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta\, e^{\pm i3\phi}$	$\mp\left(\frac{35}{64\pi}\right)^{1/2} \frac{(x \pm iy)^3}{r^3}$

[a)] Phase factor corresponding to the Condon-Shortley convention, i. e., -1 for odd positive m_l and $+1$ otherwise.

Table 12: Real orthonormal linear combinations of the spherical harmonics $Y^l_{m_l}(\theta,\phi)$ for $l = 1, 2, 3$.

l	function		designation
1	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$	$=\left(\frac{3}{4\pi}\right)^{1/2}\frac{z}{r}$	p_z
	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$	$=\left(\frac{3}{4\pi}\right)^{1/2}\frac{x}{r}$	p_x
	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$	$=\left(\frac{3}{4\pi}\right)^{1/2}\frac{y}{r}$	p_y
2	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$	$=\left(\frac{5}{16\pi}\right)^{1/2}\frac{3z^2-r^2}{r^2}$	d_{z^2}
	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$	$=\left(\frac{15}{4\pi}\right)^{1/2}\frac{xz}{r^2}$	d_{xz}
	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$	$=\left(\frac{15}{4\pi}\right)^{1/2}\frac{yz}{r^2}$	d_{yz}
	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$	$=\left(\frac{15}{16\pi}\right)^{1/2}\frac{x^2-y^2}{r^2}$	$\mathrm{d}_{x^2-y^2}$
	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$	$=\left(\frac{15}{4\pi}\right)^{1/2}\frac{xy}{r^2}$	d_{xy}
3	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$	$=\left(\frac{7}{16\pi}\right)^{1/2}\frac{z(5z^2-3r^2)}{r^3}$	f_{z^3}
	$\left(\frac{21}{32\pi}\right)^{1/2}\sin\theta(5\cos^2\theta-1)\cos\phi$	$=\left(\frac{21}{32\pi}\right)^{1/2}\frac{x(5z^2-r^2)}{r^3}$	f_{xz^2}
	$\left(\frac{21}{32\pi}\right)^{1/2}\sin\theta(5\cos^2\theta-1)\sin\phi$	$=\left(\frac{21}{32\pi}\right)^{1/2}\frac{y(5z^2-r^2)}{r^3}$	f_{yz^2}
	$\left(\frac{105}{16\pi}\right)^{1/2}\cos\theta\sin^2\theta\ \sin 2\phi$	$=\left(\frac{105}{4\pi}\right)^{1/2}\frac{xyz}{r^3}$	f_{xyz}
	$\left(\frac{105}{16\pi}\right)^{1/2}\cos\theta\sin^2\theta\ \cos 2\phi$	$=\left(\frac{105}{16\pi}\right)^{1/2}\frac{z(x^2-y^2)}{r^3}$	$\mathrm{f}_{z(x^2-y^2)}$
	$\left(\frac{35}{32\pi}\right)^{1/2}\sin^3\theta\cos 3\phi$	$=\left(\frac{35}{32\pi}\right)^{1/2}\frac{x(x^2-3y^2)}{r^3}$	$\mathrm{f}_{x(x^2-3y^2)}$
	$\left(\frac{35}{32\pi}\right)^{1/2}\sin^3\theta\sin 3\phi$	$=\left(\frac{35}{32\pi}\right)^{1/2}\frac{y(3x^2-y^2)}{r^3}$	$\mathrm{f}_{y(3x^2-y^2)}$

5.4 Angular momentum ([5]97–103)

Classical definition of angular momentum $\boldsymbol{l}$:

$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}. \tag{35}$$

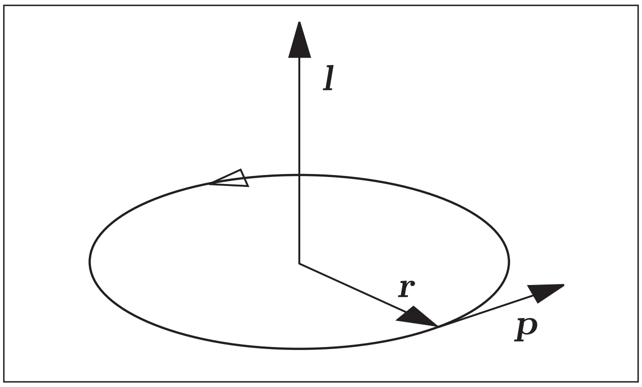


Fig. 21: Definition of the angular momentum

$$\begin{aligned} \boldsymbol{l} &= l_x \boldsymbol{i} + l_y \boldsymbol{j} + l_z \boldsymbol{k} \\ &= (y p_z - z p_y)\boldsymbol{i} + (z p_x - x p_z)\boldsymbol{j} + (x p_y - y p_x)\boldsymbol{k} \end{aligned} \tag{36}$$

Length of the angular momentum vector

$$|\boldsymbol{l}|^2 = l_x^2 + l_y^2 + l_z^2. \tag{37}$$

Derive quantum mechanical operators $\hat{l}_x$, $\hat{l}_y$, $\hat{l}_z$ by substituting the position operator and the linear momentum operator for the corresponding classical quantity, i. e.

$$q \to \hat{q} = q \cdot \qquad p_q \to \hat{p}_q = \frac{\hbar}{i}\frac{\partial}{\partial q} \qquad (q = x, y, z; \quad i = \sqrt{-1})$$

$$\hat{l}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y; \qquad \hat{l}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z; \qquad \hat{l}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \tag{38}$$

$$\hat{l}_x = \frac{\hbar}{i}\left(\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y}\right); \quad \hat{l}_y = \frac{\hbar}{i}\left(\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right); \quad \hat{l}_z = \frac{\hbar}{i}\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right) \tag{39}$$

Commutation relations

$$\boxed{[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z; \qquad [\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x; \qquad [\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y}, \tag{40}$$

Operator $\hat{l}_z$ in spherical polar coordinates:

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} \tag{41}$$

$\hat{l}_z$ acts on the ϕ depending part of the atomic orbitals (Table 11):

$$\begin{aligned}
\hat{l}_z \left| \, l \, m_l \, \right\rangle &= l_z \left| \, l \, m_l \, \right\rangle = m_l \hbar \left| \, l \, m_l \, \right\rangle \quad \text{DIRAC notation} \\
\left\langle \, l \, m_l \left| \hat{l}_z \right| l \, m_l \, \right\rangle &= m_l \, \hbar \underbrace{\left\langle \, l \, m_l \, \middle| \, l \, m_l \, \right\rangle}_{1}
\end{aligned}$$

$$\begin{aligned}
\text{generally} \quad \hat{H} \, \Psi &= E \, \Psi, \ \ (\Psi \ \text{ normalised eigenfunction of } \hat{H}) \\
\int \Psi^* \hat{H} \, \Psi \, d\tau &= E \underbrace{\int \Psi^* \, \Psi \, d\tau}_{1} \ = \ E \\
\int \Psi^* \hat{H} \, \Psi \, d\tau &\equiv \langle \Psi | \hat{H} | \Psi \rangle \quad \text{matrix element (DIRAC notation)}
\end{aligned}$$

Application of $\hat{l}_z$:

$$\begin{aligned}
\hat{l}_z \left| \, 2 \, 2 \, \right\rangle &= R_{n,2}(r) \frac{\hbar}{i} \frac{\partial Y_2^2(\theta, \phi)}{\partial \phi} \\
&= R_{n,2}(r) \frac{\hbar}{i} \frac{\partial}{\partial \phi} \left[\left(\frac{15}{32\pi} \right)^{1/2} \sin^2\theta \, e^{i2\phi} \right] \\
&= R_{n,2}(r) \frac{\hbar}{i} \left(\frac{15}{32\pi} \right)^{1/2} \sin^2\theta \, \frac{\partial e^{i2\phi}}{\partial \phi} \\
&= R_{n,2}(r) i2 \frac{\hbar}{i} \left(\frac{15}{32\pi} \right)^{1/2} \sin^2\theta \, e^{i2\phi} = 2\hbar \left| \, 2 \, 2 \, \right\rangle
\end{aligned}$$

$$\hat{\boldsymbol{l}}^2 \left| \, l \, m_l \, \right\rangle = l(l+1)\hbar^2 \left| \, l \, m_l \, \right\rangle \tag{42}$$

Shift operators:

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y; \qquad \hat{l}_- = \hat{l}_x - i\hat{l}_y. \tag{43}$$

Reverse operations:

$$\hat{l}_x = \frac{1}{2}(\hat{l}_+ + \hat{l}_-); \qquad \hat{l}_y = \frac{1}{2i}(\hat{l}_+ - \hat{l}_-). \tag{44}$$

$$\boxed{\begin{aligned}
\hat{l}_z \left| \, l \, m_l \, \right\rangle &= m_l \, \hbar \left| \, l \, m_l \, \right\rangle \\
\hat{\boldsymbol{l}}^2 \left| \, l \, m_l \, \right\rangle &= l(l+1) \, \hbar^2 \left| \, l \, m_l \, \right\rangle \\
\hat{l}_\pm \left| \, l \, m_l \, \right\rangle &= \sqrt{l(l+1) - m_l(m_l \pm 1)} \ \hbar \left| \, l \, m_l \pm 1 \, \right\rangle.
\end{aligned}} \tag{45}$$

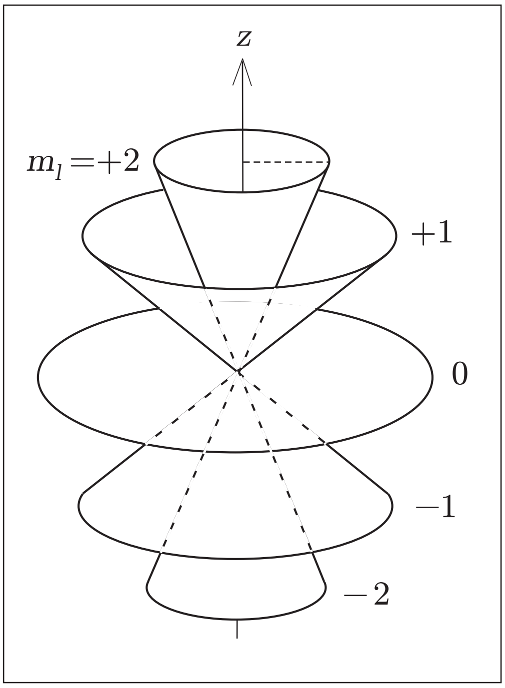


Fig. 22: Specified orientation of $\boldsymbol{l}$ ($l = 2$) with regard to the component l_z while l_x and l_y are unspecified

5.5 Spin ([5]103–105)

Spin orbital of a one-electron system:

$$\psi(\boldsymbol{r})\,\psi(\sigma) = \psi_{n,l,m_l}(r,\theta,\phi)\,\psi(\sigma) = \underbrace{R_{n,l}(r)\,Y^l_{m_l}(\theta,\phi)}_{\text{atomic orbital}}\,\psi(\sigma)$$

Spin function: $\psi(\sigma) \equiv |\, s\, m_s \,\rangle \begin{cases} m_s = \frac{1}{2}: & \alpha \\ m_s = -\frac{1}{2}: & \beta \end{cases}$

$$\boxed{\begin{array}{rcl} \hat{\boldsymbol{s}}^2 \left| s\, m_s \right\rangle & = & s(s+1)\,\hbar^2 \left| s\, m_s \right\rangle \quad \text{with} \quad s = \frac{1}{2} \\ \hat{s}_z \left| s\, m_s \right\rangle & = & m_s \hbar \left| s\, m_s \right\rangle \quad \text{with} \quad m_s = \pm\frac{1}{2} \\ \hat{s}_\pm \left| s\, m_s \right\rangle & = & \sqrt{s(s+1) - m_s(m_s \pm 1)}\;\hbar \left| s\, m_s \pm 1 \right\rangle \end{array}} \tag{46}$$

where $\quad \hat{\boldsymbol{s}}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2; \quad \hat{s}_+ = \hat{s}_x + i\hat{s}_y; \qquad \hat{s}_- = \hat{s}_x - i\hat{s}_y$

$\qquad \hat{s}_x = \frac{1}{2}(\hat{s}_+ + \hat{s}_-); \quad \hat{s}_y = \frac{1}{2i}(\hat{s}_+ - \hat{s}_-)$

5.6 Spin-orbit coupling ([5]105–116)

Spin-orbit coupling results on account of the interaction of the electron's magnetic spin moment $\boldsymbol{\mu}_s$

$$\boldsymbol{\mu}_s = -\frac{e}{2m_e} g\boldsymbol{s} = \gamma_e g\boldsymbol{s} \quad (g = 2.002\,319\,314), \quad \gamma_e \text{ magnetogyric ratio}$$

with the orbital magnetic moment at the centre of the orbit

$$\boldsymbol{\mu}_l = -\frac{e}{2m_e}\boldsymbol{l} = \gamma_e\,\boldsymbol{l}$$

caused by the circulating charged particle. Only certain orientations between $\boldsymbol{l}$ and $\boldsymbol{s}$ are allowed given by the vector sum

$$\begin{aligned} \boldsymbol{j} &= \boldsymbol{l} + \boldsymbol{s}, \quad \text{with} \begin{cases} j = l+s, l+s-1, \ldots, |l-s| \\ \text{as } \; s = 1/2 \quad \rightarrow \quad j = l \pm 1/2 \end{cases} \\ m_j &= m_l + m_s \end{aligned} \tag{47}$$

$$\hat{\boldsymbol{j}}^2 = \hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2 \qquad \hat{j}_+ = \hat{j}_x + i\hat{j}_y \qquad \hat{j}_- = \hat{j}_x - i\hat{j}_y \tag{48}$$

$$\boxed{\begin{aligned} \hat{\boldsymbol{j}}^2 \,\big|\, j\, m_j \,\big\rangle &= j(j+1)\,\hbar^2 \,\big|\, j\, m_j \,\big\rangle \\ \hat{j}_z \,\big|\, j\, m_j \,\big\rangle &= m_j\hbar \,\big|\, j\, m_j \,\big\rangle \\ \hat{j}_\pm \,\big|\, j\, m_j \,\big\rangle &= \sqrt{j(j+1) - m_j(m_j \pm 1)}\;\hbar \,\big|\, j\, m_j \pm 1 \,\big\rangle. \end{aligned}} \tag{49}$$

$$\Delta E = E(^2P_{3/2}) - E(^2P_{1/2}) = \frac{3}{2}\zeta; \qquad \text{generally:} \quad \Delta E(J, J-1) = J\,\zeta$$

Operator of spin-orbit coupling

$$\hat{H}_{so} = \xi(r)\,\hat{\boldsymbol{l}}\boldsymbol{\cdot}\hat{\boldsymbol{s}} \qquad \text{where} \qquad \xi(r) = -\frac{e}{2m_e^2c^2}\,\frac{1}{r}\,\frac{\partial V(r)}{\partial r}. \tag{50}$$

Example 5.2 *Spin-orbit coupling of the* p^1 *system*

p^1 system: $l = 1$, $s = \frac{1}{2}$, $j = \frac{1}{2}$ and $\frac{3}{2}$ (see Figs. 23 and 24, Table 13)

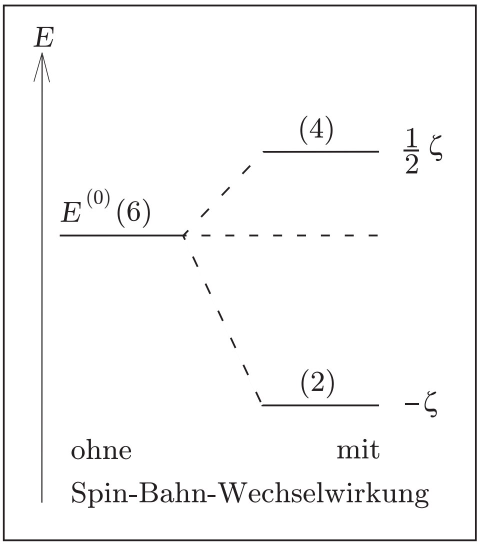


Fig. 23: Splitting of the p[1] levels by spin-orbit interaction (ζ: one-electron spin-orbit coupling constant)

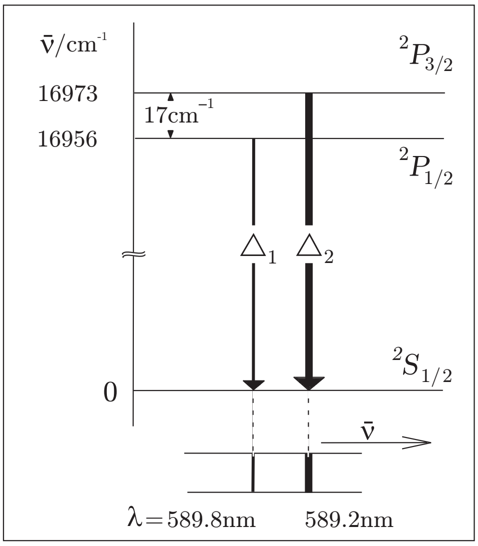


Fig. 24: Term scheme of the sodium atom

Unperturbed sixfold degenerate states:
$\hat{H}^{(0)}\psi_i^{(0)} = E^{(0)}\psi_i^{(0)} \qquad (i = 1, 2, \ldots, 6).$

Eq. (27) reads in this case:

$$(\hat{H}^{(0)} - E^{(0)})\psi^{(1)} = (E^{(1)} - \hat{H}^{(1)})\big(u_1\psi_1^{(0)} + \ldots + u_6\psi_6^{(0)}\big). \tag{51}$$

Multiplication with $\psi_1^{(0)*}$ from the left and integration gives:

$$\underbrace{\int \psi_1^{(0)*}\big(\hat{H}^{(0)} - E^{(0)}\big)\psi^{(1)}d\tau}_{0} = \int \psi_1^{(0)*}\big(E^{(1)} - \hat{H}^{(1)}\big)\big(u_1\psi_1^{(0)} + \ldots + u_6\psi_6^{(0)}\big)d\tau$$

$$\begin{aligned} 0 \;=\; & u_1E^{(1)}\int \psi_1^{(0)*}\,\psi_1^{(0)}d\tau + \ldots + u_6E^{(1)}\int \psi_1^{(0)*}\,\psi_6^{(0)}d\tau \\ & -u_1\int \psi_1^{(0)*}\,\hat{H}^{(1)}\,\psi_1^{(0)}d\tau - \ldots - u_6\int \psi_1^{(0)*}\,\hat{H}^{(1)}\,\psi_6^{(0)}d\tau. \end{aligned} \tag{52}$$

Proceeding similarly with $\psi_i^{(0)*}$ $(i = 2, \ldots, 6)$ and using the abbreviation $\int \psi_i^{(0)*}\hat{H}^{(1)}\psi_j^{(0)}d\tau \equiv H_{ij}$ we obtain a system of six equations:

$$\begin{aligned} 0 &= u_1\big(H_{11} - E^{(1)}\big) + u_2H_{12} + \cdots + u_6H_{16} \\ 0 &= u_1H_{21} + u_2\big(H_{22} - E^{(1)}\big) + \cdots + u_6H_{26} \\ \vdots & \qquad\qquad \vdots \\ 0 &= u_1H_{61} + u_2H_{62} + \cdots + u_6\big(H_{66} - E^{(1)}\big) \end{aligned} \tag{53}$$

Non-trivial solutions for the coefficients of $u_1, u_2, \ldots, u_6$:
Calculation of the integrals H_{ij}

$$\int \big(\psi_{n,l,m_l}(r,\theta,\phi)\,\psi_{m_s}(\sigma)\big)^*\,\hat{H}_{SB}\,\psi_{n,l,m_l'}(r,\theta,\phi)\,\psi_{m_s'}(\sigma)\,r^2\,dr\,\sin\theta\,d\theta\,d\phi\,d\sigma. \tag{54}$$

$$\begin{aligned}&\int_0^\infty R_{n,l}(r)\,\xi(r)\,R_{n,l}(r)\,r^2\,dr \;\times \\ &\quad\int_0^\pi\int_0^{2\pi}\int_{-1/2}^{1/2}\big(Y_l^{m_l}(\theta,\phi)\,\psi_{m_s}(\sigma)\big)^*\,\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}\,\big(Y_l^{m_l'}(\theta,\phi)\,\psi_{m_s'}(\sigma)\big)\sin\theta\,d\theta\,d\phi\,d\sigma.\end{aligned} \tag{55}$$

$$hc\,\zeta_{n,l} = \hbar^2\int_0^\infty R_{n,l}(r)\,\xi(r)\,R_{n,l}(r)\,r^2\,dr. \tag{56}$$

$\zeta_{n,l}$: one-electron spin-orbit coupling constant
basis functions in Dirac notation: $\big|\,m_l\,m_s\big\rangle$

$$\big|\,1\,\tfrac{1}{2}\big\rangle \quad \big|\,0\,\tfrac{1}{2}\big\rangle \quad \big|\,-1\,\tfrac{1}{2}\big\rangle \quad \big|\,1\,-\tfrac{1}{2}\big\rangle \quad \big|\,0\,-\tfrac{1}{2}\big\rangle \quad \big|\,-1\,-\tfrac{1}{2}\big\rangle. \tag{57}$$

The integral eq. (55) has the short form

$$\frac{hc\zeta_{n,l}}{\hbar^2}\big\langle m_l\,m_s\big|\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}\big|\,m_l'\,m_s'\big\rangle. \tag{58}$$

Determination of 36 matrix elements of the spin-orbit coupling operator $\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}} \;=\; \hat{l}_x\hat{s}_x + \hat{l}_y\hat{s}_y + \hat{l}_z\hat{s}_z$.
Replace the x and y components by the step operators (eq. (44,46)):

$$\begin{aligned}\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}} &= \hat{l}_z\hat{s}_z + \tfrac{1}{2}(\hat{l}_+ + \hat{l}_-)\tfrac{1}{2}(\hat{s}_+ + \hat{s}_-) + \tfrac{1}{2i}(\hat{l}_+ - \hat{l}_-)\tfrac{1}{2i}(\hat{s}_+ - \hat{s}_-) \\ &= \hat{l}_z\hat{s}_z + \tfrac{1}{4}(\hat{l}_+\hat{s}_+ + \hat{l}_-\hat{s}_+ + \hat{l}_+\hat{s}_- + \hat{l}_-\hat{s}_- \\ &\qquad\quad -\hat{l}_+\hat{s}_+ + \hat{l}_-\hat{s}_+ + \hat{l}_+\hat{s}_- - \hat{l}_-\hat{s}_-) \\ &= \hat{l}_z\hat{s}_z + \tfrac{1}{2}(\hat{l}_+\hat{s}_- + \hat{l}_-\hat{s}_+)\end{aligned} \tag{59}$$

The general matrix element (58) is

$$\begin{aligned}\big\langle m_l\,m_s\big|\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}\big|\,m_l'\,m_s'\big\rangle &= \big\langle m_l\,m_s\big|\hat{l}_z\hat{s}_z + \tfrac{1}{2}(\hat{l}_+\hat{s}_- + \hat{l}_-\hat{s}_+)\big|\,m_l'\,m_s'\big\rangle \\ &= \big\langle m_l\,m_s\big|\hat{l}_z\hat{s}_z\big|\,m_l'\,m_s'\big\rangle \\ &\quad +\tfrac{1}{2}\big\langle m_l\,m_s\big|\hat{l}_+\hat{s}_-\big|\,m_l'\,m_s'\big\rangle \\ &\quad +\tfrac{1}{2}\big\langle m_l\,m_s\big|\hat{l}_-\hat{s}_+\big|\,m_l'\,m_s'\big\rangle.\end{aligned} \tag{60}$$

General hints to the evaluation of matrix elements $\big\langle m\big|\hat{H}^{(1)}\big|n\big\rangle$:

(i) Evaluate $\hat{H}^{(1)}\big|n\big\rangle$. This will result in a constant a multiplied by a wavefunction which may or may not be the same as the original. For the present let us assume $\hat{H}^{(1)}\big|n\big\rangle = a\big|n\big\rangle$.
(ii) The result of (i) is then premultiplied by $\big\langle m\big|$ giving $\big\langle m\big|an\big\rangle$.
(iii) Since a is a constant we have $\big\langle m\big|an\big\rangle = a\big\langle m\big|n\big\rangle$ and we are thus left with the task of evaluating $\big\langle m\big|n\big\rangle$. Provided $\big|m\big\rangle$ and $\big|n\big\rangle$ are orthonormalised, $\big\langle m\big|n\big\rangle = 1$ when $m = n$ but is zero otherwise.
On account of orthonormalised states

$$\big\langle m_l\, m_s\big|\, m_l'\, m_s'\big\rangle = \delta_{m_l,m_l'}\,\delta_{m_s,m_s'}, \tag{61}$$

the integral is not zero when $m_l = m_l'$ and $m_s = m_s'$. The wavefunctions are eigenfunctions of $\hat{l}_z$ und $\hat{s}_z$, so that the application of the operator products in eq. (60) on the wavefunction on its right-hand side yields:

$$\begin{aligned}
\hat{l}_z\hat{s}_z\,\big|\,m_l\,m_s\big\rangle &= m_l\,m_s\,\hbar^2\,\big|\,m_l\,m_s\big\rangle \\
\hat{l}_+\hat{s}_-\,\big|\,m_l\,m_s\big\rangle &= \\
&\sqrt{l(l+1)-m_l(m_l+1)}\sqrt{s(s+1)-m_s(m_s-1)}\,\hbar^2\,\big|\,m_l+1\,m_s-1\big\rangle \\
\hat{l}_-\hat{s}_+\,\big|\,m_l\,m_s\big\rangle &= \\
&\sqrt{l(l+1)-m_l(m_l-1)}\sqrt{s(s+1)-m_s(m_s+1)}\,\hbar^2\,\big|\,m_l-1\,m_s+1\big\rangle
\end{aligned}$$

where $s = \frac{1}{2}$. For diagonal elements only $\hat{l}_z\hat{s}_z$ may contribute, whereas for non-diagonal elements only the step operators may account:

$$\big\langle m_l\,m_s\big|\hat{l}_+\hat{s}_-\big|\,m_l-1\,m_s+1\big\rangle \qquad \big\langle m_l\,m_s\big|\hat{l}_-\hat{s}_+\big|\,m_l+1\,m_s-1\big\rangle$$

Matrix elements (58) which may contribute are restricted to the condition

$$m_l + m_s = m_l' + m_s' \tag{62}$$

The non-zero matrix elements are:

$$\begin{array}{ll}
\big\langle\,1\;-\tfrac{1}{2}\,\big|\hat{l}_+\hat{s}_-\big|\,0\;\tfrac{1}{2}\,\big\rangle & \big\langle\,0\;-\tfrac{1}{2}\,\big|\hat{l}_+\hat{s}_-\big|-1\,\tfrac{1}{2}\,\big\rangle \\
\big\langle\,0\;\tfrac{1}{2}\big|\hat{l}_-\hat{s}_+\big|\,1\;-\tfrac{1}{2}\,\big\rangle & \big\langle\,-1\,\tfrac{1}{2}\,\big|\hat{l}_-\hat{s}_+\big|\,0\;-\tfrac{1}{2}\big\rangle.
\end{array}$$

(63)

$m_l m_s$	$\|1\ \frac{1}{2}\rangle$	$\|1\ -\frac{1}{2}\rangle$	$\|0\ \frac{1}{2}\rangle$	$\|0\ -\frac{1}{2}\rangle$	$\|-1\ \frac{1}{2}\rangle$	$\|-1\ -\frac{1}{2}\rangle$
$\langle 1\ \frac{1}{2}\|$	$\frac{1}{2}\zeta$					
$\langle 1\ -\frac{1}{2}\|$		$-\frac{1}{2}\zeta$	$\sqrt{\frac{1}{2}}\zeta$			
$\langle 0\ \frac{1}{2}\|$		$\sqrt{\frac{1}{2}}\zeta$	0			
$\langle 0\ -\frac{1}{2}\|$				0	$\sqrt{\frac{1}{2}}\zeta$	
$\langle -1\ \frac{1}{2}\|$				$\sqrt{\frac{1}{2}}\zeta$	$-\frac{1}{2}\zeta$	
$\langle -1\ -\frac{1}{2}\|$						$\frac{1}{2}\zeta$

$$
\begin{aligned}
H_{11} &= \frac{\zeta}{\hbar^2}\left\langle 1\ \tfrac{1}{2}\right|\hat{l}_z\hat{s}_z\left|1\ \tfrac{1}{2}\right\rangle = \zeta\cdot 1\cdot\tfrac{1}{2}\left\langle 1\ \tfrac{1}{2}\middle|1\ \tfrac{1}{2}\right\rangle = \tfrac{1}{2}\zeta \\
H_{22} &= \frac{\zeta}{\hbar^2}\left\langle 1\ -\tfrac{1}{2}\right|\hat{l}_z\hat{s}_z\left|1\ -\tfrac{1}{2}\right\rangle = \zeta\cdot 1\cdot(-\tfrac{1}{2}) = -\tfrac{1}{2}\zeta \\
H_{33} &= \frac{\zeta}{\hbar^2}\left\langle 0\ \tfrac{1}{2}\right|\hat{l}_z\hat{s}_z\left|0\ \tfrac{1}{2}\right\rangle = \zeta\cdot 0\cdot\tfrac{1}{2} = 0 \\
H_{44} &= \frac{\zeta}{\hbar^2}\left\langle 0\ -\tfrac{1}{2}\right|\hat{l}_z\hat{s}_z\left|0\ -\tfrac{1}{2}\right\rangle = \zeta\cdot 0\cdot(-\tfrac{1}{2}) = 0 \\
H_{55} &= \frac{\zeta}{\hbar^2}\left\langle -1\ \tfrac{1}{2}\right|\hat{l}_z\hat{s}_z\left|-1\ \tfrac{1}{2}\right\rangle = \zeta\cdot(-1)\cdot\tfrac{1}{2} = -\tfrac{1}{2}\zeta \\
H_{66} &= \frac{\zeta}{\hbar^2}\left\langle -1\ -\tfrac{1}{2}\right|\hat{l}_z\hat{s}_z\left|-1\ -\tfrac{1}{2}\right\rangle = \zeta\cdot(-1)\cdot(-\tfrac{1}{2}) = \tfrac{1}{2}\zeta \\
H_{23} &= \frac{\zeta}{\hbar^2}\left\langle 1\ -\tfrac{1}{2}\right|\tfrac{1}{2}\hat{l}_+\hat{s}_-\left|0\ \tfrac{1}{2}\right\rangle = \tfrac{1}{2}\zeta\cdot\sqrt{2}\cdot 1\left\langle 1\ -\tfrac{1}{2}\middle|1\ -\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{1}{2}}\,\zeta = H_{32} \\
H_{45} &= \frac{\zeta}{\hbar^2}\left\langle 0\ -\tfrac{1}{2}\right|\tfrac{1}{2}\hat{l}_+\hat{s}_-\left|-1\ \tfrac{1}{2}\right\rangle = \tfrac{1}{2}\zeta\cdot\sqrt{2}\cdot 1 = \sqrt{\tfrac{1}{2}}\,\zeta = H_{54}
\end{aligned}
$$

Diagonalisation of the 2×2 blocks of the H matrix:

$$
\begin{aligned}
\begin{vmatrix} -\frac{1}{2}\zeta - E^{(1)} & \sqrt{\frac{1}{2}}\,\zeta \\ \sqrt{\frac{1}{2}}\,\zeta & -E^{(1)} \end{vmatrix} &= (-\tfrac{1}{2}\zeta - E^{(1)})(-E^{(1)}) - \tfrac{1}{2}\zeta^2 = 0 \\
E^{(1)}_{(1)} &= \tfrac{1}{2}\zeta; \qquad\qquad E^{(1)}_{(2)} = -\zeta.
\end{aligned}
$$

Evaluation of the zeroth-order functions for $E^{(1)}_{(1)} = \frac{1}{2}\zeta$:

$$
0 = \left(-\tfrac{1}{2}\zeta - \tfrac{1}{2}\zeta\right)u_{2(1)} + \sqrt{\tfrac{1}{2}}\,\zeta\, u_{3(1)}
$$

$$
\begin{aligned}
x_{(1)} &= \frac{u_{2(1)}}{u_{3(1)}} = \sqrt{\tfrac{1}{2}}; \qquad u_{2(1)} = \sqrt{\tfrac{1}{3}}; \qquad u_{3(1)} = \sqrt{\tfrac{2}{3}} \\
\psi_2 &= \sqrt{\tfrac{1}{3}}\,\big|\,1\ -\tfrac{1}{2}\,\big\rangle + \sqrt{\tfrac{2}{3}}\,\big|\,0\ \tfrac{1}{2}\,\big\rangle. \qquad (64)
\end{aligned}
$$

For $E^{(1)}_{(2)} = -\zeta$, the result is:

$$
\begin{aligned}
0 &= \left(-\tfrac{1}{2}\,\zeta + \zeta\right) u_{2(2)} + \sqrt{\tfrac{1}{2}}\,\zeta\, u_{3(2)} \\
x_{(2)} &= \frac{u_{2(2)}}{u_{3(2)}} = -\sqrt{2}; \qquad u_{2(2)} = -\sqrt{\tfrac{2}{3}}; \qquad u_{3(2)} = \sqrt{\tfrac{1}{3}} \\
\psi_3 &= -\sqrt{\tfrac{2}{3}}\,\big|\,1\ -\tfrac{1}{2}\,\big\rangle + \sqrt{\tfrac{1}{3}}\,\big|\,0\ \tfrac{1}{2}\,\big\rangle. \qquad (65)
\end{aligned}
$$

Evaluating the second 2×2 block the resulting states are

$$
\begin{aligned}
E^{(1)}_{(1)} = \tfrac{1}{2}\,\zeta: \qquad \psi_4 &= \sqrt{\tfrac{1}{3}}\,\big|\,-1\,\tfrac{1}{2}\,\big\rangle + \sqrt{\tfrac{2}{3}}\,\big|\,0\ -\tfrac{1}{2}\,\big\rangle \qquad (66) \\
E^{(1)}_{(2)} = -\zeta: \qquad \psi_5 &= \sqrt{\tfrac{2}{3}}\,\big|\,-1\,\tfrac{1}{2}\,\big\rangle - \sqrt{\tfrac{1}{3}}\,\big|\,0\ -\tfrac{1}{2}\,\big\rangle. \qquad (67)
\end{aligned}
$$

The functions are not only eigenfunctions of the operators $\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}$ and $\hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{l}}$ but also of

$$
\hat{\boldsymbol{l}}^{\,2} + \hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}} + \hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{l}} + \hat{\boldsymbol{s}}^2 = \big(\hat{\boldsymbol{l}} + \hat{\boldsymbol{s}}\big)^2 = \hat{\boldsymbol{j}}^2. \qquad (68)
$$

If $\hat{\boldsymbol{j}}^2$ acts on a quartet state function ψ_Q $(\psi_1, \psi_2, \psi_4, \psi_6)$ and on a doublet state function ψ_D (ψ_3, ψ_5), respectively the result is

$$
\begin{aligned}
\hat{\boldsymbol{j}}^2\,\psi_Q &= \big(\hat{\boldsymbol{l}}^{\,2} + 2\,\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}} + \hat{\boldsymbol{s}}^2\big)\,\psi_Q \\
&= \hbar^2\left(2 + 2\cdot\tfrac{1}{2} + \tfrac{3}{4}\right)\psi_Q = \hbar^2\,(\tfrac{15}{4})\,\psi_Q = \hbar^2\,(\tfrac{3}{2})(\tfrac{5}{2})\,\psi_Q \\
&= \hbar^2\,j_1(j_1+1)\,\psi_Q \qquad \text{where} \quad j_1 = \tfrac{3}{2} \qquad (69) \\
\hat{\boldsymbol{j}}^2\,\psi_D &= \big(\hat{\boldsymbol{l}}^{\,2} + 2\,\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}} + \hat{\boldsymbol{s}}^2\big)\,\psi_D \\
&= \hbar^2\left(2 - 2\cdot 1 + \tfrac{3}{4}\right)\psi_D = \hbar^2\,(\tfrac{3}{4})\,\psi_D = \hbar^2\,(\tfrac{1}{2})(\tfrac{3}{2})\,\psi_D \\
&= \hbar^2\,j_2(j_2+1)\,\psi_D \qquad \text{where} \quad j_2 = \tfrac{1}{2}. \qquad (70)
\end{aligned}
$$

Table 13: Functions and energies of the p^1 system

ψ	$\lvert m_l\, m_s \rangle$	$\lvert j\, m_j \rangle$	$m_j = m_l + m_s$	j	$E^{(1)}$
ψ_1	$\lvert 1\ \frac{1}{2} \rangle$	$\lvert \frac{3}{2}\ \frac{3}{2} \rangle$	$\frac{3}{2}$		
ψ_2	$\sqrt{\frac{1}{3}} \lvert 1\ -\frac{1}{2} \rangle + \sqrt{\frac{2}{3}} \lvert 0\ \frac{1}{2} \rangle$	$\lvert \frac{3}{2}\ \frac{1}{2} \rangle$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}\zeta$
ψ_4	$\sqrt{\frac{1}{3}} \lvert -1\ \frac{1}{2} \rangle + \sqrt{\frac{2}{3}} \lvert 0\ -\frac{1}{2} \rangle$	$\lvert \frac{3}{2}\ -\frac{1}{2} \rangle$	$-\frac{1}{2}$		
ψ_6	$\lvert -1\ -\frac{1}{2} \rangle$	$\lvert \frac{3}{2}\ -\frac{3}{2} \rangle$	$-\frac{3}{2}$		
ψ_3	$-\sqrt{\frac{2}{3}} \lvert 1\ -\frac{1}{2} \rangle + \sqrt{\frac{1}{3}} \lvert 0\ \frac{1}{2} \rangle$	$\lvert \frac{1}{2}\ \frac{1}{2} \rangle$	$\frac{1}{2}$	$\frac{1}{2}$	$-\zeta$
ψ_5	$\sqrt{\frac{2}{3}} \lvert -1\ \frac{1}{2} \rangle - \sqrt{\frac{1}{3}} \lvert 0\ -\frac{1}{2} \rangle$	$\lvert \frac{1}{2}\ -\frac{1}{2} \rangle$	$-\frac{1}{2}$		

Example: Energy eigenvalues and eigenfunctions of $4f^1$ (Ce^{3+}) and $4f^{13}$ (Yb^{3+})

On account of $j = l \pm s = 3 \pm \frac{1}{2}$ (eqn. (47)) for one-electron and one-hole f systems we have

$Ln^{3+}[4f^N]$	ground multiplet	E	excited multiplet	E
$Ce^{3+}[4f^1]$	${}^2F_{5/2}\,(j = 5/2)$	$-2\zeta_{\mathrm{Ce}}$	${}^2F_{7/2}\,(j = 7/2)$	$+\frac{3}{2}\zeta_{\mathrm{Ce}}$
$Yb^{3+}[4f^{13}]$	${}^2F_{7/2}\,(j = 7/2)$	$-\frac{3}{2}\zeta_{\mathrm{Yb}}$	${}^2F_{5/2}\,(j = 5/2)$	$+2\zeta_{\mathrm{Yb}}$

Eigenfunctions are obtained with the help of so-called *vector coupling coefficients* (Clebsch-Gordan coefficients) (see Table 14).

Table 14: Vector coupling coefficients for systems with $j_2 = 1/2$

$j =$	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\sqrt{\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$
$j_1 - \frac{1}{2}$	$-\sqrt{\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$

Table 15: Spin-orbit coupled eigenfunctions of Ce^{3+} and Yb^{3+} free ions

$^{a)}$	$\lvert j\, m_j \rangle$ $\quad \lvert m_l\, m_s \rangle$	$E_J^{(Ce^{3+})}$	$E_J^{(Yb^{3+})}$
$\phi_1; \phi_6$	$\lvert \frac{5}{2} \pm\frac{5}{2} \rangle = \mp\sqrt{\frac{6}{7}}\,\lvert \pm 3 \mp\frac{1}{2} \rangle \pm \sqrt{\frac{1}{7}}\,\lvert \pm 2 \pm\frac{1}{2} \rangle$		
$\phi_2; \phi_5$	$\lvert \frac{5}{2} \pm\frac{3}{2} \rangle = \mp\sqrt{\frac{5}{7}}\,\lvert \pm 2 \mp\frac{1}{2} \rangle \pm \sqrt{\frac{2}{7}}\,\lvert \pm 1 \pm\frac{1}{2} \rangle$	-2ζ	2ζ
$\phi_3; \phi_4$	$\lvert \frac{5}{2} \pm\frac{1}{2} \rangle = \mp\sqrt{\frac{4}{7}}\,\lvert \pm 1 \mp\frac{1}{2} \rangle \pm \sqrt{\frac{3}{7}}\,\lvert 0 \pm\frac{1}{2} \rangle$		
$\phi'_1; \phi'_8$	$\lvert \frac{7}{2} \pm\frac{7}{2} \rangle = \lvert \pm 3 \pm\frac{1}{2} \rangle$		
$\phi'_2; \phi'_7$	$\lvert \frac{7}{2} \pm\frac{5}{2} \rangle = \sqrt{\frac{1}{7}}\,\lvert \pm 3 \mp\frac{1}{2} \rangle + \sqrt{\frac{6}{7}}\,\lvert \pm 2 \pm\frac{1}{2} \rangle$	$\frac{3}{2}\zeta$	$-\frac{3}{2}\zeta$
$\phi'_3; \phi'_6$	$\lvert \frac{7}{2} \pm\frac{3}{2} \rangle = \sqrt{\frac{2}{7}}\,\lvert \pm 2 \mp\frac{1}{2} \rangle + \sqrt{\frac{5}{7}}\,\lvert \pm 1 \pm\frac{1}{2} \rangle$		
$\phi'_4; \phi'_5$	$\lvert \frac{7}{2} \pm\frac{1}{2} \rangle = \sqrt{\frac{3}{7}}\,\lvert \pm 1 \mp\frac{1}{2} \rangle + \sqrt{\frac{4}{7}}\,\lvert 0 \pm\frac{1}{2} \rangle$		

$^{a)}$ Short form of the functions: the first symbol refers to the upper sign, the second to the lower one.

The calculation of the coefficients is demonstrated for $\lvert \frac{5}{2}\,\frac{5}{2} \rangle$ (first line in Table 15).
Assignments: $j = 5/2$, $m = m_j = 5/2$, $j_1 = l = 3$, and $m_2 = m_s = \pm 1/2$ $(j_2 = s = 1/2)$
The roots of the lower row of Table 14 become

$$m_2 = -\frac{1}{2}: \quad \sqrt{\frac{j_1 + m + \frac{1}{2}}{2j_1 + 1}} = \sqrt{\frac{3 + \frac{5}{2} - \frac{1}{2}}{7}} = \sqrt{\frac{6}{7}}$$

$$m_2 = \frac{1}{2}: \quad -\sqrt{\frac{j_1 - m + \frac{1}{2}}{2j_1 + 1}} = \sqrt{\frac{3 - \frac{5}{2} + \frac{1}{2}}{7}} = -\sqrt{\frac{1}{7}}$$

Since the CONDON-SHORTLEY standard assignment is $j_1 \to s$ and $j_2 \to l$ the sign of the coefficients has to be changed according to the phase relation $|j_b j_a j m\rangle = (-1)^{j_a + j_b - j} |j_a j_b j m\rangle$. Finally, we obtain
$\lvert \frac{5}{2}\,\frac{5}{2} \rangle = -\sqrt{\frac{6}{7}}\,\lvert 3 - \frac{1}{2} \rangle + \sqrt{\frac{1}{7}}\,\lvert 2 + \frac{1}{2} \rangle$.

Problems

1. Calculate the matrix elements $\langle l, m_l | \hat{l}_q | l, m_l' \rangle$ (where q stands for $z, +, -$) (a) $\langle 0, 0 | \hat{l}_z | 0, 0 \rangle$, (b) $\langle 2, 2 | \hat{l}_+ | 2, 1 \rangle$, (c) $\langle 2, 2 | \hat{l}_+^2 | 2, 0 \rangle$, (d) $\langle 2, 0 | \hat{l}_+ \hat{l}_- | 2, 0 \rangle$.

2. The 14 microstates $|m_l m_s\rangle$ of an f^1 system ($l = 3$, $s = 1/2$) yield under the influence of the spin-orbit coupling operator 14 eigenstates $|j m_j\rangle$ which are linear combinations of the microstates. Use Table 14 to evaluate the vector coupling coefficients for the coupled states $|5/2 \;\; 1/2\rangle$, $|5/2 \;\; -1/2\rangle$, $|7/2 \;\; 3/2\rangle$, and $|7/2 \;\; -3/2\rangle$. Control your results with the entries of Table 15.

6 Exchange interactions in dinuclear compounds

6.1 Parametrization of exchange interactions

- Heitler-London model of H_2

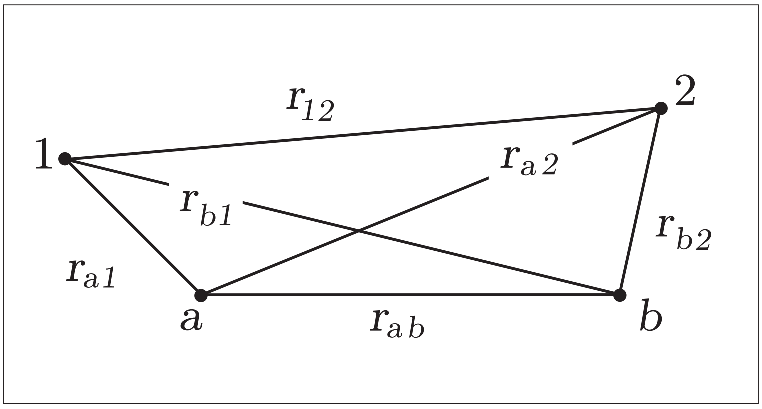


Fig. 25: H_2 model; a and b assign the nuclei, 1 and 2 the electrons

Valence bond ansatz: construction of products with orbital configuration $\phi_a\phi_b$ using the four spin orbitals

$$\phi_a\alpha \qquad \phi_a\beta \qquad \phi_b\alpha \qquad \phi_b\beta$$

Product states in consideration of the Pauli principle:

$$D_1 = \phi_a(1)\alpha(1)\,\phi_b(2)\beta(2) - \phi_a(2)\alpha(2)\,\phi_b(1)\beta(1) \tag{71}$$
$$D_2 = \phi_a(1)\beta(1)\,\phi_b(2)\alpha(2) - \phi_a(2)\beta(2)\,\phi_b(1)\alpha(1) \tag{72}$$
$$D_3 = \phi_a(1)\alpha(1)\,\phi_b(2)\alpha(2) - \phi_a(2)\alpha(2)\,\phi_b(1)\alpha(1) \tag{73}$$
$$D_4 = \phi_a(1)\beta(1)\,\phi_b(2)\beta(2) - \phi_a(2)\beta(2)\,\phi_b(1)\beta(1) \tag{74}$$

- *Construction of eigenfunctions of the total spin*

$\hat{\boldsymbol{S}}' = \hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2 \quad (S_1 = S_2 = 1/2)$

D_3 and D_4 are eigenfunctions $|\, S'\, M'_S \,\rangle$ of $\hat{\boldsymbol{S}}'^2 = (\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2)^2$ and $\hat{S}'_z = \hat{S}_{z1} + \hat{S}_{z2}$ with $S' = 1$ and $M_{S'} = 1$ and -1 (Spin triplet functions $|\,1\,1\,\rangle$ and $|\,1\,{-1}\,\rangle$), respectively.
$D_1 + D_2 \Longrightarrow |\,1\,0\,\rangle$ (spin triplet function)
$D_1 - D_2 \Longrightarrow |\,0\,0\,\rangle$ (spin singlet function)

$$\begin{array}{cccc} \Phi_1 = D_1 - D_2 & \Phi_2 = D_3 & \Phi_3 = D_1 + D_2 & \Phi_4 = D_4 \\ |\,0\,0\,\rangle & |\,1\,1\,\rangle & |\,1\,0\,\rangle & |\,1\,{-1}\,\rangle \end{array}$$

ϕ_a and ϕ_b are normalised:

$$\int \phi_a(1)^* \phi_a(1) d\tau_1 = \int \phi_b^*(2)\phi_b(2) d\tau_2 = 1,$$

but not orthogonal:

$$\textit{overlap integral} \quad S_{ab} = \int \phi_a(1)^* \phi_b(1) d\tau_1 = \int \phi_a(2)^* \phi_b(2) d\tau_2 \neq 0$$

Normalised functions of the dinuclear unit:

$$\Phi_1 = N_g \underbrace{[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]}_{\text{sym}} \underbrace{\sqrt{\tfrac{1}{2}}\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}_{\text{anti}}$$

$$\left.\begin{array}{c} \Phi_2 \\ \Phi_3 \\ \Phi_4 \end{array}\right\} = N_u \underbrace{[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]}_{\text{anti}} \underbrace{\left\{\begin{array}{l} \alpha(1)\alpha(2) \\ \sqrt{\tfrac{1}{2}}\,[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\ \beta(1)\beta(2) \end{array}\right.}_{\text{sym}}$$

where $N_g = [2 + 2S_{ab}^2]^{-\frac{1}{2}}$ and $N_u = [2 - 2S_{ab}^2]^{-\frac{1}{2}}$.

- *Symmetry of the functions with regard to exchange of electrons*

total function:	anti $\quad \Phi_i(1,2) = -\Phi_i(2,1)$
singlet function:	orbital sym (g), spin function anti
triplet functions:	orbital anti (u), spin function sym

$\Longrightarrow$ Symmetry of the orbital forces a distinct multiplicity of the spin function on account of the PAULI principle

- *Evaluation of the energy $E(S)$ and $E(T)$ of the singlet and triplet states*

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2(1) - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{b1}}}_{\hat{h}(1)} \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2(2) - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b2}}}_{\hat{h}(2)} + \frac{e^2}{r_{12}}$$

$$E(S) = \langle {}^1\Phi_1^g|\hat{H}|{}^1\Phi_1^g\rangle = \frac{2(h + h_{ab}S_{ab}) + J_{ab} + K_{ab}}{1 + S_{ab}^2} \tag{75}$$

$$E(T) = \langle {}^3\Phi_2^u|\hat{H}|{}^3\Phi_2^u\rangle = \frac{2(h - h_{ab}S_{ab}) + J_{ab} - K_{ab}}{1 - S_{ab}^2} \tag{76}$$

where

$$\begin{aligned}
h &= \left\langle \phi_a(i) \left| \hat{h}(i) \right| \phi_a(i) \right\rangle \quad \text{(one-centre} \\
&= \left\langle \phi_b(i) \left| \hat{h}(i) \right| \phi_b(i) \right\rangle \quad \text{one-electron integral)} \\
h_{ab} &= \left\langle \phi_a(i) \left| \hat{h}(i) \right| \phi_b(i) \right\rangle \quad \text{(transfer or hopping integral)} \\
J_{ab} &= \left\langle \phi_a(1)\phi_b(2) \left| e^2/r_{12} \right| \phi_a(1)\phi_b(2) \right\rangle \quad \text{(COULOMB integral)} \\
K_{ab} &= \left\langle \phi_a(1)\phi_b(2) \left| e^2/r_{12} \right| \phi_a(2)\phi_b(1) \right\rangle \quad \text{(Exchange integral).}
\end{aligned}$$

Example: Evaluation of $E(S) = \left\langle {}^1\Phi_1^g \middle| \hat{H} \middle| {}^1\Phi_1^g \right\rangle$

1. Integration over the spin:

$$\begin{aligned}
&\tfrac{1}{2}\langle\alpha(1)\beta(2) - \beta(1)\alpha(2)|\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle = \\
&\qquad \tfrac{1}{2}\big[\underbrace{\langle\alpha(1)\beta(2)|\alpha(1)\beta(2)\rangle}_{1} + \underbrace{\langle\alpha(2)\beta(1)|\alpha(2)\beta(1)\rangle}_{1} - \\
&\qquad \underbrace{\langle\alpha(2)\beta(1)|\alpha(1)\beta(2)\rangle}_{0} - \underbrace{\langle\alpha(1)\beta(2)|\alpha(2)\beta(1)\rangle}_{0}\big] = 1.
\end{aligned}$$

2. Integration over the space:

$$\begin{aligned}
&E(S) = \\
&N_g^2 \left\langle \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) \middle| \hat{h}(1) + \hat{h}(2) + e^2/r_{12} \middle| \phi_a(1)\phi_b(2) + \right. \\
&\qquad \left. \phi_b(1)\phi_a(2) \right\rangle = 2N_g^2[2(h + h_{ab}S_{ab}) + J_{ab} + K_{ab}].
\end{aligned} \tag{77}$$

Singlet-triplet splitting:

$$\begin{aligned}
\Delta E(T,S) &= E(T) - E(S) \\
&\approx -2K_{ab} - 4h_{ab}S_{ab} + 2S_{ab}^2(2h + J_{ab})
\end{aligned}$$

- *Application of the* Heitler-London *model to dinuclear complexes having* $S_1 = S_2 = \frac{1}{2}$ *centres*

Example: $\mathrm{L'_nCu_a{-}L{-}Cu_bL'_n}$

As distinguished from the strong covalent bond in H_2 the interactions between both magnetically active electrons is weak.

$\Longrightarrow$ small $\Delta E(T,S)$.

The highest singly occupied antibonding orbitals ϕ_a and ϕ_b of the fragments $\mathrm{L'_nCu_aL}$ and $\mathrm{LCu_bL'_n}$, respectively take over the role of the 1s orbitals of the H atoms. ϕ_a and ϕ_b have mainly d character. They are centered at the metal ions and partially delocalised in the direction of the ligands.

6.2 Heisenberg operator

Phenomenological description of the interaction between the unpaired electrons of the centres by an *apparent spin-spin coupling*, whose magnitude and sign are given by the spin-spin coupling parameter (exchange parameter) $\mathcal{J}$:

$$\boxed{\hat{H}_{ex} = -2\mathcal{J}\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2 \quad \text{where} \quad -2\mathcal{J} = \Delta E(T,S)} \tag{78}$$

$\hat{H}_{ex}$ is an *effective* operator, describing but not explaining the phenomenon.

Application of $\hat{H}_{ex}$ to ${}^1\Phi_1^g$ ($S'=0$) and ${}^3\Phi_i^u$ ($S'=1, i=2,3,4$):

$$-2\mathcal{J}\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2\,{}^1\Phi_1^g = \underbrace{\left(\tfrac{3}{2}\right)\mathcal{J}}_{E(S)}\,{}^1\Phi_1^g, \qquad -2\mathcal{J}\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2\,{}^3\Phi_i^u = \underbrace{-\left(\tfrac{1}{2}\right)\mathcal{J}}_{E(T)}\,{}^3\Phi_i^u$$

$$\Longrightarrow \quad \Delta E(T,S) = E(T) - E(S) = -2\mathcal{J} \tag{79}$$

$\mathcal{J} < 0$: singlet ground state (intramolecular antiferromagnetic interaction)
$\mathcal{J} > 0$: triplet ground state (intramolecular ferromagnetic interaction)

Hints to the evaluation of $E(T)$ and $E(S)$:

$$\begin{aligned}
\hat{\boldsymbol{S}}'^2 &= \left(\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2\right)^2 = \hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + 2\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2\\
2\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2 &= \hat{\boldsymbol{S}}'^2 - \hat{\boldsymbol{S}}_1^2 - \hat{\boldsymbol{S}}_2^2\\
&= \hbar^2\big[\underbrace{S'(S'+1)}_{0 \text{ or } 2} - \underbrace{S_1(S_1+1)}_{\frac{3}{4}} - \underbrace{S_2(S_2+1)}_{\frac{3}{4}}\big]
\end{aligned}$$

Heisenberg operator for more than two centres:

$$\hat{H}_{ex} = -2\sum_{i<j}\mathcal{J}_{ij}\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j \tag{80}$$

$$\hat{H}_{ex} = -2\mathcal{J}\sum_{i<j}\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_j \tag{81}$$

Magnetic susceptibility ([5]138–162)
Fundamental magnetisation equation

$$\boxed{M_{mol} = -N_A\frac{\sum_n(\partial E_n/\partial B)\exp(-E_n/k_BT)}{\sum_n\exp(-E_n/k_BT)} = N_A\frac{\sum_n\bar{\mu}_n\exp(-E_n/k_BT)}{\sum_n\exp(-E_n/k_BT)}}$$

$$(82)$$

Van Vleck **equation**

Operator: $\hat{H} = \hat{H}^{(0)} + B_z \hat{H}^{(1)}$

$E_n = W_n^{(0)} + B_z W_n^{(1)} + B_z^2 W_n^{(2)} + \dots .$

$W_n^{(1)}$, $W_n^{(2)}$: First- and second-orderZeeman coefficients

$\bar{\mu}_n = -\partial E_n / \partial B = -W_n^{(1)} - 2BW_n^{(2)} - \dots$

$$\boxed{\chi_{mol} = \mu_0 N_A \frac{\sum\limits_n [(W_n^{(1)})^2 / k_B T - 2W_n^{(2)}] \exp(-W_n^{(0)}/k_B T)}{\sum\limits_n \exp(-W_n^{(0)}/k_B T)}} \quad (83)$$

Eq. (83) is valid for applied magnetic fields $B \to 0$

6.3 Exchange-coupled species in a magnetic field

$$\begin{aligned} \hat{H}_{ex} &= -2\mathcal{J}\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 = -2\mathcal{J}\left(\hat{S}_{z1}\hat{S}_{z2} + \hat{S}_{x1}\hat{S}_{x2} + \hat{S}_{y1}\hat{S}_{y2}\right) \\ &= -2\mathcal{J}\left[\hat{S}_{z1}\hat{S}_{z2} + \tfrac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-2} + \hat{S}_{-1}\hat{S}_{+2}\right)\right] \end{aligned} \quad (84)$$

Basis: spin functions in the form $|\, M_S \, M_S \,\rangle$ where the first M_S refers to electron 1 and the second to electron 2
H-Matrix:

$$(85)$$

$M_{S_1} M_{S_2}$	$\vert\, \frac{1}{2}\ \frac{1}{2} \,\rangle$	$\vert -\frac{1}{2}\ \frac{1}{2} \,\rangle$	$\vert\, \frac{1}{2} -\frac{1}{2} \,\rangle$	$\vert -\frac{1}{2}\ -\frac{1}{2} \,\rangle$
$\langle\, \frac{1}{2}\ \frac{1}{2} \,\vert$	$-\mathcal{J}/2$			
$\langle -\frac{1}{2}\ \frac{1}{2} \,\vert$		$\mathcal{J}/2$	$-\mathcal{J}$	
$\langle\, \frac{1}{2}\ -\frac{1}{2} \,\vert$		$-\mathcal{J}$	$\mathcal{J}/2$	
$\langle -\frac{1}{2}\ -\frac{1}{2} \,\vert$				$-\mathcal{J}/2$

Evaluation of the diagonal element H_{11}:

$-2\mathcal{J}\langle\, \frac{1}{2}\ \frac{1}{2} \,|\, \hat{S}_{z1}\hat{S}_{z2} \,|\, \frac{1}{2}\ \frac{1}{2} \,\rangle = -2\mathcal{J}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) = -\mathcal{J}/2$

Evaluation of the off-diagonal element H_{23}:

$$-2\mathcal{J}\left\langle -\tfrac{1}{2}\ \tfrac{1}{2} \,\middle|\, \tfrac{1}{2}\hat{S}_{-1}\hat{S}_{+2} \,\middle|\, \tfrac{1}{2}\ -\tfrac{1}{2} \right\rangle = -\mathcal{J}(1)(1) = -\mathcal{J}$$

Result:

Tab. 16: Spin functions and exchange energies of the $S_1 = S_2 = \frac{1}{2}$ system

Spin function	$M_{S'}$	S'	E
$\frac{1}{\sqrt{2}}\left(\left\|\, \frac{1}{2}\ -\frac{1}{2} \right\rangle - \left\|\, -\frac{1}{2}\ \frac{1}{2} \right\rangle\right)$	0	0	$\frac{3}{2}\mathcal{J}$
$\left\|\, \frac{1}{2}\ \frac{1}{2} \right\rangle$	1		
$\frac{1}{\sqrt{2}}\left(\left\|\, \frac{1}{2}\ -\frac{1}{2} \right\rangle + \left\|\, -\frac{1}{2}\ \frac{1}{2} \right\rangle\right)$	0	1	$-\frac{1}{2}\mathcal{J}$
$\left\|\, -\frac{1}{2}\ -\frac{1}{2} \right\rangle$	-1		

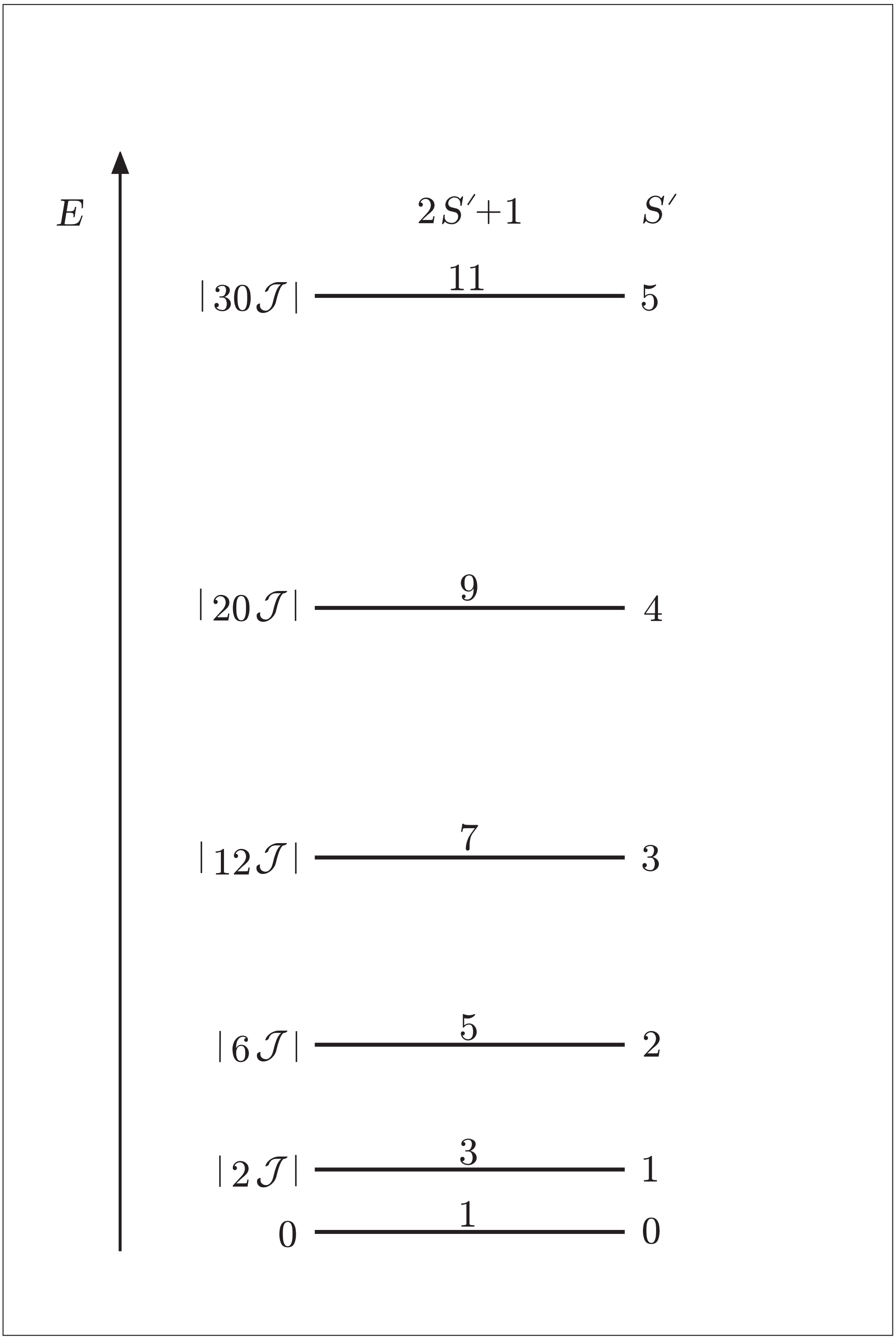


Fig. 26: Relative energies and multiplicities of the spin states of a dinuclear Fe^{3+} complex ($S = \frac{5}{2}$); for Cu^{2+} ($S = \frac{1}{2}$) only the two lowest levels are relevant, while for Gd^{3+} ($S = \frac{7}{2}$) the two levels with $S' = 6$ ($E = |42\mathcal{J}|$) and $S' = 7$ ($E = |56\mathcal{J}|$) have to be added.

- *Magnetic susceptibility of a spin-spin-coupled system with* $S_1 = S_2 = \frac{1}{2}$

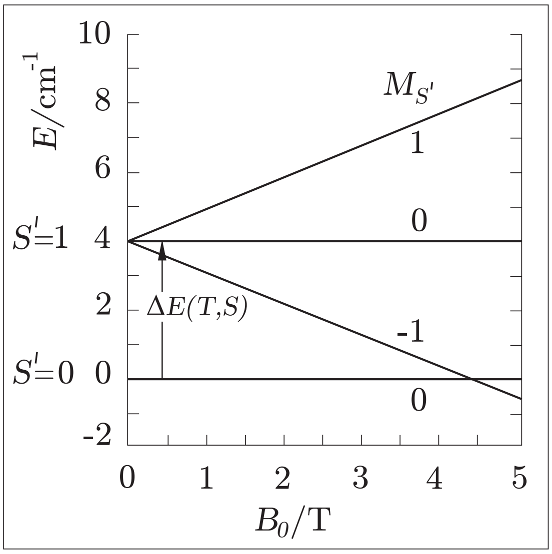


Fig. 27: Correlation diagram of a $S_1 = S_2 = \frac{1}{2}$ system under the influence of isotropic intramolecular spin-spin coupling ($\mathcal{J} = -2\,\mathrm{cm}^{-1}$) and applied field

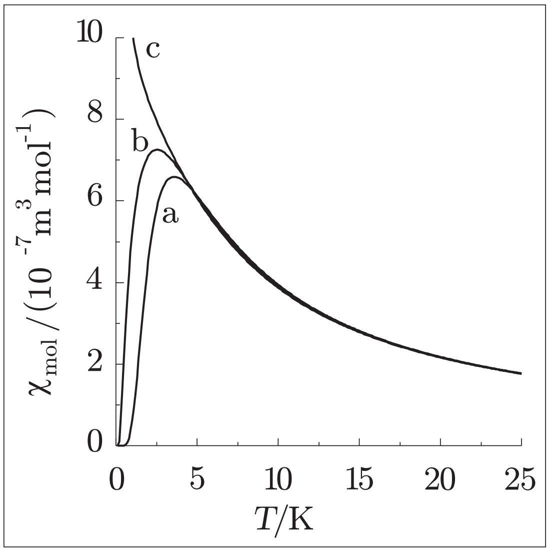


Fig. 28: χ_{mol} *versus* T diagram of a $S_1 = S_2 = \frac{1}{2}$ exchange-coupled system with $\mathcal{J} = -2\,\mathrm{cm}^{-1}$ at applied fields of $B_0 = 0.01\,\mathrm{T}$ (a), $3.5\,\mathrm{T}$ (b), and $5\,\mathrm{T}$ (c)

Application of the Van Vleck equation (83) to a dinuclear system with $S_1 = S_2 = \frac{1}{2}$
Zeeman-Operator:

$$\hat{H}_{M_z} = \underbrace{-\gamma_e g(\hat{S}_{z1} + \hat{S}_{z2})}_{\hat{H}^{(1)}} B_z = -\gamma_e\, g\, \hat{S}'_z\, B_z \tag{86}$$

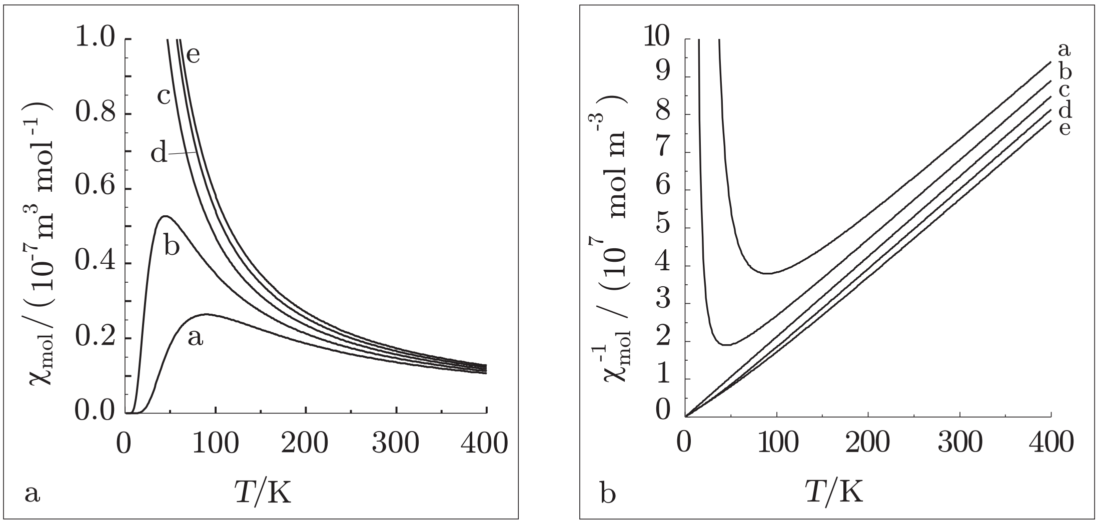
$S' M_{S'}$	$\vert 1\,1\rangle$	$\vert 1\,0\rangle$	$\vert 1\,-1\rangle$	$\vert 0\,0\rangle$
$\langle 1\,1\vert$	$g\mu_B B_z$			
$\langle 1\,0\vert$		0		
$\langle 1\,-1\vert$			$-g\mu_B B_z$	
$\langle 0\,0\vert$				0

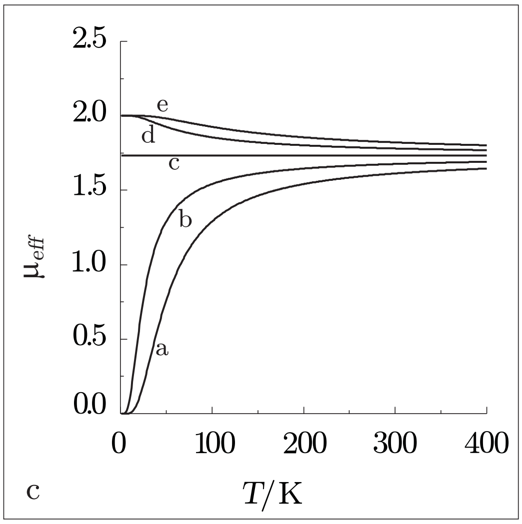
Matrix elements:

$$\begin{aligned}\langle 11|\hat{H}_{M_z}|11\rangle &= g\mu_B B_z \longrightarrow W^{(1)}_{|11\rangle} = g\mu_B \\ \langle 1\,-1|\hat{H}_{M_z}|1\,-1\rangle &= -g\mu_B B_z \longrightarrow W^{(1)}_{|1-1\rangle} = -g\mu_B\end{aligned}$$

The remaining matrix elements (ZEEMAN coefficients) are zero. $W^{(1)}_{|11\rangle}$, $W^{(1)}_{|1-1\rangle}$, $W^{(0)}_S = E(S)$, and $W^{(0)}_T = E(T)$ are substituted into the VAN VLECK equation. After dividing by 2, the BLEANEY-BOWERS expression (χ_{mol} per centre) is obtained, here extended by χ_0

$$\chi_{mol} = \mu_0 \frac{N_A \mu_B^2 g^2}{3k_B T}\left[1 + \frac{1}{3}\exp\left(\frac{-2\mathcal{J}}{k_B T}\right)\right]^{-1} + \chi_0, \quad \text{only applicable to a (Fig. 28)} \tag{87}$$





Model calculations concerning the system $S_1 = S_2 = \frac{1}{2}$ with positive and negative $\mathcal{J}$;

$\mathcal{J}$ values [cm^{-1}]:
curve a: -50
curve b: -25
curve c: 0
curve d: $+25$
curve e: $+50$

Fig. 29 a: χ_{mol}–T diagram
Fig. 29 b: χ^{-1}_{mol}–T diagram
Fig. 29 c: μ_{eff}–T diagram

Polynuclear unit of n equivalent centres:

$$\boxed{\chi_{mol} = \frac{\mu_0}{n}\frac{N_A\mu_B^2 g^2}{3k_BT}\frac{\sum_{S'} S'(S'+1)(2S'+1)\Omega(S')\exp\left(-\frac{E(S')}{k_BT}\right)}{\sum_{S'}(2S'+1)\Omega(S')\exp\left(-\frac{E(S')}{k_BT}\right)}} \tag{88}$$

Evaluation of S', $E(S')$ and $\Omega(S')$:

S' of the coupled states:
$S' = nS, nS-1, \ldots, 0$ (nS integer) or $\frac{1}{2}$ (nS half integer)

Relative energies $E(S')$:

$$E(S') = -\frac{z\mathcal{J}}{n-1}\left[S'(S'+1) - nS(S+1)\right]$$

z: number of nearest neighbours of a centre
n: number of interacting centres

Frequency $\Omega(S')$ of the states S':

$$\Omega(S') = \omega(S') - \omega(S'+1)$$

$\omega(S')$ is the coefficient of $X^{S'}$ in the expansion

$$(X^S + X^{S-1} + \ldots + X^{-S})^n$$

- *Scope of validity of the* Heisenberg *model*

1. Localised magnetic moments (no band magnetism)
2. *good* quantum number S of the centres
3. orbital singlet as ground term
   $3d^5$-High-Spin $\longrightarrow {}^6A_1$
   $3d^3(O_h)$, $3d^7(T_d) \longrightarrow {}^4A_2$
   $3d^8(O_h)$, $3d^2(T_d) \longrightarrow {}^3A_2$
   ($3d^9(O_h) \longrightarrow {}^2E$)

6.4 Mechanisms of cooperative magnetic effects in insulators

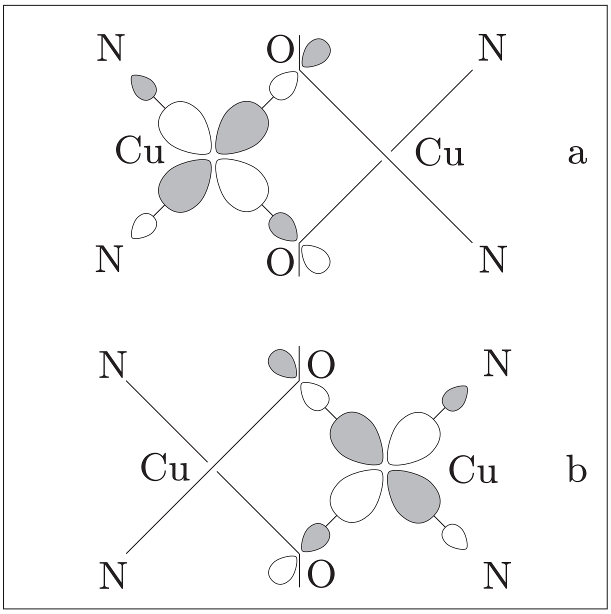


Fig. 30: Magnetic orbitals *a* and *b*, localised in the left and right fragment of $[L_2'Cu_2(\mu\text{-}OH)_2]^{2+}$ (Kahn,1993)

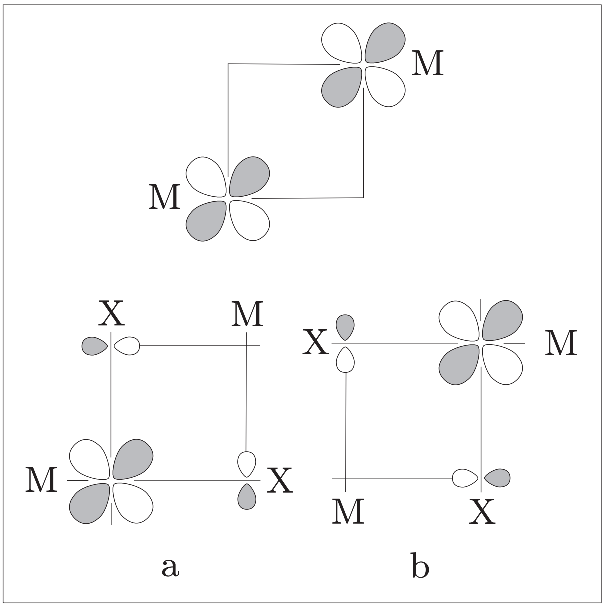


Fig. 31: $CrCl_3$, $CrBr_3$: Magnetic orbitals; top: direct exchange d_{xy}–d'_{xy}; bottom: 90° superexchange

Problems

1. Verify the equation $\hat{\boldsymbol{S}}^2 = \hat{S}_z^2 - \hbar\hat{S}_z + \hat{S}_+\hat{S}_-$.

2. Show, that the function eq. (74)

   $$\Psi_4 = D_4 = \phi_a(1)\beta(1)\,\phi_b(2)\beta(2) - \phi_a(2)\beta(2)\,\phi_b(1)\beta(1)$$

   is an eigenfunction of $\hat{\boldsymbol{S}}'^2 = (\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2)^2$ and $\hat{S}'_z = \hat{S}_{z1} + \hat{S}_{z2}$! How large are S' and $M_{S'}$?

3. Corresponding to $E(S)$, eq. (77), evaluate the energy $E(T)$ of the triplet state and verify the result given in eq. (76).

4. Reconstruct the steps eq. (86) $\longrightarrow$ eq. (87).

5. The Bleaney-Bowers formula, eq. (87), approaches for high temperature the Curie-Weiss law, eq. (9). Give the relation between $\mathcal{J}$ and Θ_p. Is the result in agreement with the right formula in eq. (9)?

6. What magnetic behaviour is obtained, if in the Bleaney-Bowers-Formel, eq. (87), $\mathcal{J}$ is set to 0?

7. Determine on the basis of matrix (85) and perturbation theory the correct zeroth-order wavefunctions and verify the entries in Table 16.

8. Write the Heisenberg spin operator for a trinuclear unit of equivalent centres (equilateral triangle). What spin operator applies for an isosceles triangle and what operator for a three-membered chain?

9. What general formula evaluates the magnetic susceptibility of an equilateral triangle? The derivation of the susceptibility expression for an isosceles triangle needs more expense. What steps have to be considered if perturbation theory is consequently applied? Give the basis functions (spin functions) for a $S_1 = S_2 = S_3 = \frac{1}{2}$ system. What are the resulting S' states? What operator represents the perturbation by the magnetic field?

10. Give a rough drawing of the χ_{mol}^{-1}–T diagram of a homotrinuclear cluster with equivalent antiferromagnetically coupled $S = \frac{1}{2}$ centres. (Hint: Think what magnetic behaviour is expected for high and low temperature, $k_BT \gg |\mathcal{J}|$ and $k_BT \ll |\mathcal{J}|$, respectively.)

11. Magnetochemical results are often presented as χ_{mol}–T, χ_{mol}^{-1}–T or μ_{eff}–T diagrams. What type of diagram is suited for (a) CURIE paramagnetism, (b) intramolecular ferromagnetic interactions, (c) intramolekular antiferromagnetic interactions, (d) diamagnetic behaviour, (e) TUP behaviour?

12. To reliably characterise magnetic properties measurements at different field strength are essential. What is the reason?

13. A frequent mistake in magnetochemical investigations is the application of too strong magnetic fields. Why may this be unfavourable?

14. To evaluate the paramagnetic part of the susceptibility of a compound with macrocyclic ligands, the problem may occur that the incremental method for the diamagnetic correction is not as precise as necessary. What is to be done?

15. For a polynuclear complex one observes at high temperature CURIE-WEISS behaviour with $\Theta_p > 0$ and in the low-temperature region field-dependent susceptibilities. What magnetic collective effects can be expected?

16. With decreasing temperature the μ_{eff} data of a homodinuclear compound increase weakly and then, after passing a maximum at low temperature, steeply drop. What is the reason for this behaviour? What model (susceptibility expression) should be tried to simulate the behaviour?

17. You notice that the paramagnetic properties of a dinuclear centrosymmetric molecular compound is not satisfactorily described with the corresponding eq. (88). What extensions of the model are in principle possible?

18. The homodinuclear complex [Cp*RuCl$_2$] (Ru^{III}[4d^5], low spin, $S = 1/2$) contains in the unit cell two isomeric forms (ratio 1:1) with distinctly different Ru–Ru separations of 2.93 and 3.75 Å. Give a rough drawing of μ_{eff} as a function of T assuming that the Ru centres in the former are antiferromagnetically coupled with $\mathcal{J} \leq -400\,\mathrm{cm}^{-1}$ while in the latter the centres are coupled ferromagnetically with $\mathcal{J} = 12\,\mathrm{cm}^{-1}$.

7 Exchange interactions in chain compounds

Uniform chain

$$\overset{\mathcal{J}}{\text{———}}\ \mathrm{M_i}\ \overset{\mathcal{J}}{\text{———}}\ \mathrm{M}_{i+1}\ \overset{\mathcal{J}}{\text{———}}\ \mathrm{M}_{i+2}\ \overset{\mathcal{J}}{\text{———}}$$

$$\hat{H} = -2\mathcal{J}\sum_{i=1}^{N-1}\hat{\boldsymbol{S}}_i\cdot\hat{\boldsymbol{S}}_{i+1} - \gamma_e g B_z \sum_{i=1}^{N}\hat{S}_{i,z}, \tag{89}$$

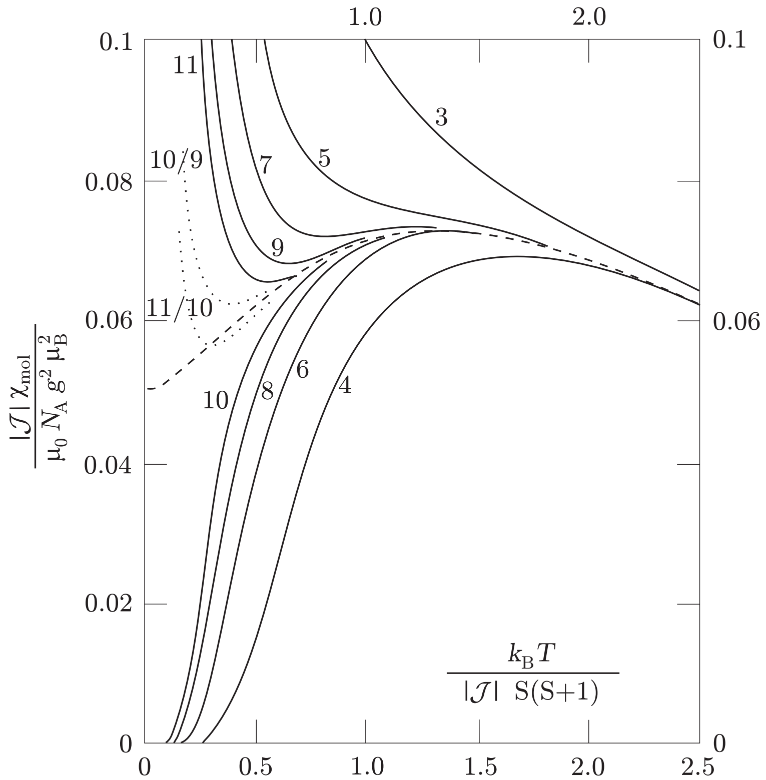


Fig. 32: Temperature dependent magnetic susceptibility (reduced units) of an $S = 1/2$ antiferromagnetically coupled 1 D system (Heisenberg model)

Simulation of the magnetic susceptibility for infinite chains of Cu(II):

$$\chi_{mol} = \mu_0 \frac{N_A g^2 \mu_B^2}{k_B T}\frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \tag{90}$$

with $x = |2\mathcal{J}|/(k_B T)$.
Susceptibility equation for classical spins, i. e., spins without space quantization

$$\chi_{mol} = \mu_0 \frac{N_A \mu_B^2 g^2 S(S+1)}{3k_B T}\frac{1+u}{1-u} \text{ with } u = \coth\left[\frac{2\mathcal{J}S(S+1)}{k_B T}\right] - \frac{k_B T}{2\mathcal{J}S(S+1)}. \tag{91}$$

Tab. 17: Compounds with 1 D arrangements of magnetic exchange-coupled centres

compound	S	bridge	$\mathcal{J}$ [cm^{-1}]	$\mathcal{J}'$ [cm^{-1}]$^{a)}$
$Cu(C_2O_4) \cdot \frac{1}{3} H_2O$	$\frac{1}{2}$	$C_2O_4^{2-}$	-146	
$(C_6H_{11}NH_3)CuCl_3$	$\frac{1}{2}$	$(\mu\text{-}Cl)_2$	50	$0.05, -10^{-2}$
$CuGeO_3$	$\frac{1}{2}$	O^{2-}	-63	$-6; 0.6$
$CsNiCl_3$	1	Cl^-	-9	$^{b)}$

$^{a)}$ $\mathcal{J}$: 'intrachain' parameter; $\mathcal{J}'$: 'interchain' parameter.
$^{b)}$ $|\mathcal{J}'/\mathcal{J}| = 7 \times 10^{-3}$.

Alternating chain

$$\overset{\mathcal{J}}{\text{——}}\ \mathrm{M}_i\ \overset{\alpha\mathcal{J}}{\text{——}}\ \mathrm{M}_{i+1}\ \overset{\mathcal{J}}{\text{——}}\ \mathrm{M}_{i+2}\ \overset{\alpha\mathcal{J}}{\text{——}}$$

The HEISENBERG operator reads in this case

$$\hat{H}_{ex} = -2\mathcal{J} \sum_{i=1}^{N} \left(\hat{\boldsymbol{S}}_{2i} \cdot \hat{\boldsymbol{S}}_{2i-1} + \alpha \hat{\boldsymbol{S}}_{2i} \cdot \hat{\boldsymbol{S}}_{2i+1} \right) . \tag{92}$$

For $\alpha = 0$ the model reduces to homodinuclear systems. For antiferromagnetic couplings with $\alpha \neq 0$ (except $\alpha = 1$) the magnetic susceptibility decreases to zero for $T \to 0$.

Chains with chain links –Cu^{2+}–L–Mn^{2+}– of antiferromagnetically coupled Cu(II)–Mn(II) are important as intermediate stage towards spontaneously magnetised molecular 3 D systems.

8 Exchange interactions in layers and 3 D networks

8.1 Molecular-field model ([5] 330-350)

The simplest and most naïve effective field approximation consists in considering only one magnetic atom and replacing its interaction with the remainder of the crystal by an effective field. It is assumed that the effective field, the so-called molecular field, is proportional to the average magnetisation of the compound:

$$\boldsymbol{H}_{MF} = \lambda_{MF} \boldsymbol{M}_{mol} \quad \text{with} \quad \lambda_{MF} = \frac{2 \sum_i^n z_i \mathcal{J}_i}{\mu_0 N_A \mu_B^2 g_J^2} . \tag{93}$$

λ is positive for ferromagnetic and negative for antiferromagnetic interactions. In the presence of an applied field H, the total field acting on the centre is

$$H_{eff} = H + H_{MF}. \tag{94}$$

Owing to the molecular field, the paramagnetic behaviour ($T > T_C(T_N)$) is modified:

$$\begin{aligned} M_{mol} &= \chi'_{mol}(H + H_{MF}) \;=\; \chi'_{mol}(H + \lambda M_{mol}) \\ M_{mol}/H &= \chi_{mol} \;=\; \chi'_{mol}(1 + \lambda \chi_{mol}) \\ \chi_{mol}^{-1} &= (\chi'_{mol})^{-1} - \lambda. \end{aligned} \tag{95}$$

λ produces a parallel shift of the $(\chi'_{mol})^{-1}$–T curve. If the isolated centre obeys the CURIE law, the CURIE-WEISS law is obtained:

$$\chi_{mol}^{-1} = \frac{T}{C} - \lambda \quad \Longrightarrow \quad \chi_{mol} = \frac{C}{T - \Theta_p} \quad \text{where} \quad \Theta_p = \lambda C. \tag{96}$$

λ and Θ_p have the same sign. Positive and negative Θ_p values refer to predominating ferro- and antiferromagnetic interactions, respectively. The layer-type compound $FeCl_2$ may serve as an example that is magnetically characterised by dominating ferromagnetic intralayer and weaker antiferromagnetic interlayer interactions. This does lead to $\Theta_p > 0$, but an antiferromagnetic spin structure is observed below T_N.

For pure spin systems Θ_p and the spin-spin coupling parameters $\mathcal{J}_i$ are related by

$$\Theta_p = \frac{2S(S+1)}{3k_B} \sum_{i}^{n} z_i \mathcal{J}_i, \tag{97}$$

where z_i is the number of i^{th} nearest neighbours of a given magnetic centre, $\mathcal{J}_i$ stands for the exchange interaction between the i^{th} neighbours and n is the number of sets of neighbours for which $\mathcal{J}_i \neq 0$.

The molecular field approximation is applicable to ferromagnetic, antiferromagnetic, and ferrimagnetic materials below and above the critical temperature $T_C(T_N)$ [5].

8.2 High-temperature series expansion (HTSE); ([5] 386 – 415)

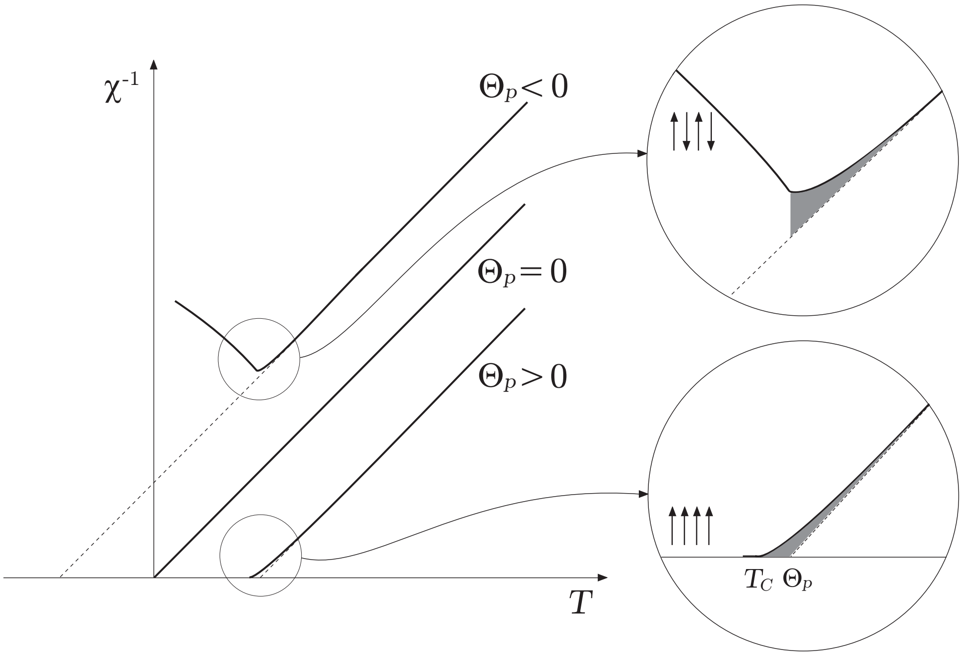


Fig. 33: Schematic representation (shaded area) of the deviation from CURIE-WEISS behaviour

$$\chi_{mol} = \mu_0 N_A g \gamma_e \frac{\partial}{\partial B} \left\{ \frac{Tr\left[\sum_i \hat{S}_{zi} \exp\left(-\hat{H}\beta\right)\right]}{Z} \right\}, \qquad \beta \equiv 1/(k_B T)$$

$$\boxed{\hat{H} = -2\mathcal{J} \sum_{i<j} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j - g\gamma_e B_z \sum_i \hat{S}_{zi}}$$

$$\exp(-\beta\hat{H}) = 1 - (\beta\hat{H}) + \frac{(\beta\hat{H})^2}{2!} - \ldots = \sum_{k=0}^{\infty} \frac{1}{k!}(-\beta\hat{H})^k$$

$$\boxed{\chi_{mol}(B \to 0) = \mu_0 \frac{N_A g^2 \gamma_e^2}{k_B T} \frac{Tr\left\{ \sum_i \hat{S}_{zi} \sum_j \hat{S}_{zj} \sum_{k=0}^{\infty} \frac{(2\beta\mathcal{J})^k}{k!} \left[\sum_{i<j} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j\right]^k \right\}}{Tr\left\{ \sum_{k=0}^{\infty} \frac{(2\beta\mathcal{J})^k}{k!} \left[\sum_{i<j} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j\right]^k \right\}}}$$

Example: $CrBr_3$ (space group $R\overline{3}$), $T_C = 32.7\,\mathbf{K}$

$$\hat{H}_{ex} = -2\mathcal{J}_1 \sum_{<i,j>}^{1.n} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j - 2\underbrace{\alpha\mathcal{J}_1}_{\mathcal{J}_2} \sum_{<k,l>}^{2.n} \hat{\boldsymbol{S}}_k \cdot \hat{\boldsymbol{S}}_l - 2\underbrace{\beta\mathcal{J}_1}_{\mathcal{J}_3} \sum_{<m,n>}^{3.n} \hat{\boldsymbol{S}}_m \cdot \hat{\boldsymbol{S}}_n$$

$$\chi_{mol} \;=\; \frac{C}{T}\left[1 + \sum_{t=1}^{\infty} a_t \left(\frac{\mathcal{J}_1}{k_B T}\right)^t\right] \quad \text{with} \quad a_t = \sum_{r+s\leq t} a'_{t-r-s,r,s}\alpha^r\beta^s$$

Results

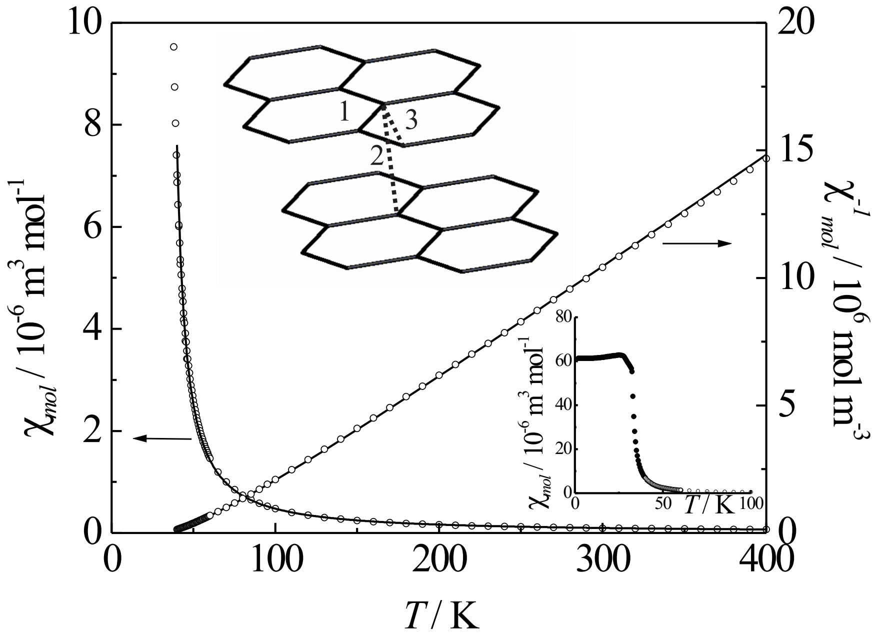


Fig. 34: Cr^{3+} ($S = 3/2$) partial structure in $CrBr_3$ and χ_{mol} and χ^{-1}_{mol} as a function of temperature (applied field: $B_0 = 0.1\,\mathrm{T}$); the solid lines refer to the HTSE model with $g = 1.952$, $J_1 = 6.900\ \mathrm{cm}^{-1}$, $J_2 = 0\ \mathrm{cm}^{-1}$ (fixed), $J_3 = -0.080\ \mathrm{cm}^{-1}$ (quality of the fit: $SQ = 0.7\,\%$; $SQ = (FQ/n)^{1/2} \times 100\%$, with $FQ = \sum_{i=1}^{n} \{[\chi_{obs}(i) - \chi_{cal}(i)]/\chi_{obs}(i)\}^{1/2}$)

Parameter	g	$\mathcal{J}_1$ [cm^{-1}]	$\mathcal{J}_2$ [cm^{-1}]	$\mathcal{J}_3$ [cm^{-1}]
d(Cr–Cr) [pm]		364	612	631
susceptibility	1.952	6.90	$0 \rightarrow 0.60$	$-0.08 \rightarrow -0.19$
spin wave analysis		6.85	≈ 0	-0.115

9 Magnetochemical analysis in practice

1. use g as parameter (in addition to $\mathcal{J}$)

2. if necessary use χ_0 (TIP) as parameter:

   $$\chi_{mol} = \chi'_{mol} + \chi_0 \tag{98}$$

   χ'_{mol}: polynuclear unit

3. Intermolecular cooperative interactions, weak compared to the intramolecular interaction:

   $$\frac{1}{\chi_{mol}} = \frac{1}{\chi'_{mol}} - \lambda \tag{99}$$

   λ: molecular field parameter

4. Intermolecular cooperative interactions, competing with the intramolecular exchange interaction:
   application of higher-dimensional models in the framework of high-temperature series expansions ($CrBr_3$)

5. Mononuclear impurity:

   $$\chi_{mol} = (1-\rho)\chi'_{mol} + \rho\,\frac{C}{T-\Theta_p} \tag{100}$$

   Use ρ, C, Θ_p as parameters (in addition to g und $\mathcal{J}$)

6. Spinfrustration: Observed in the case of antiferromagnetic interactions, if the topology does not allow a satisfactory antiparallel spin-spin coupling for all centres (example: tetranuclear rhombic unit with antiferromagnetic interactions in the direction of the edges as well as in the direction of the short diagonal)

7. Publication of magnetochemical results:
   indication of the spin operator (definition of $\mathcal{J}$),
   χ^{dia}_{mol}, ΔT, B_0, number of magnetic centres

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Appendix

Tab. 18: Energy conversion factors

	J	eV	s^{-1}	cm^{-1}	K	T	kJ/mol
1 J	1	6,24151 $\times10^{18}$	1,50919 $\times10^{33}$	5,03411 $\times10^{22}$	7,24292 $\times10^{22}$	1,07828 $\times10^{23}$	6,02214 $\times10^{20}$
1 eV	1,60218 $\times10^{-19}$	1	2,41799 $\times10^{14}$	8,06554 $\times10^{3}$	1,16045 $\times10^{4}$	1,72760 $\times10^{4}$	9,64853 $\times10^{1}$
1 s^{-1}	6,62607 $\times10^{-34}$	4,13567 $\times10^{-15}$	1	3,33564 $\times10^{-11}$	4,79922 $\times10^{-11}$	7,14477 $\times10^{-11}$	3,99031 $\times10^{-13}$
1 cm^{-1}	1,98645 $\times10^{-23}$	1,23984 $\times10^{-4}$	2,99792 $\times10^{10}$	1	1,43877	2,14195	1,19626 $\times10^{-2}$
1 K	1,38066 $\times10^{-23}$	8,61739 $\times10^{-5}$	2,08367 $\times10^{10}$	6,95039 $\times10^{-1}$	1	1,48874	8,31451 $\times10^{-3}$
1 T	9,27402 $\times10^{-24}$	5,78839 $\times10^{-5}$	1,39963 $\times10^{10}$	4,66864 $\times10^{-1}$	6,71710 $\times10^{-1}$	1	5,58494 $\times10^{-3}$
1 kJ/mol	1,66054 $\times10^{-21}$	1,03642 $\times10^{-2}$	2,50607 $\times10^{12}$	8,35933 $\times10^{1}$	1,20272 $\times10^{2}$	1,79053 $\times10^{2}$	1