Course of lectures on magnetism of lanthanide ions under varying ligand and magnetic fields

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1 Magnetic properties of free lanthanide ions: an overview

1.1 Electronic structure and Hund’s rules

The 4f electrons of free Ln ions are influenced by nuclear attraction, interelectronic repulsion \(H_{ee}\) and spin-orbit coupling \(H_{SO}\), where \(H_{ee} > H_{SO}\). To determine the free ion ground multiplet \(2S + 1L_J\) the following scheme is helpful \((N: \text{no. of 4f electrons})\):

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

1. The term with maximum \(S\) lies lowest in energy \((\sum_i m_{s,i} = M_S \rightarrow S)\).

2. For a given spin multiplicity, the term with highest \(L\) lies lowest in energy \((\sum_i m_{l,i} = M_L \rightarrow L)\).

3. For less than half-filled subshells, the level with the lowest value of \(J\) lies lowest \((J = |L - S|)\), while the highest \(J\) lies lowest when a subshell is more than half full \((J = L + S)\).

Examples: \(\text{Pr}^{3+} [4f^2]\): \(S = 1, \quad L = 5, \quad J = 4; \quad (^3H_4)\)

\(\text{Dy}^{3+} [4f^9]\): \(S = \frac{5}{2}, \quad L = 5, \quad J = \frac{15}{2}; \quad (^6H_{15/2})\)

1.2 Energetic effects

The energy splittings of the electronic states of a magnetic system\(^1\) are produced by \(H_{ee}\), \(H_{SO}\), the ligand field \((H_{LF})\), interatomic exchange interactions \((H_{ex})\), and the applied magnetic field \((H_{mag})\). The following scheme shows the order of \(H_{ee}, H_{SO}, H_{LF}\).

\[
\begin{array}{ccc|c}
3d^N & H_{ee} & H_{LF} & H_{SO} & \text{weak field} \\
H_{LF} & > & H_{ee} & > & H_{SO} & \text{strong field} \\
H_{LF} & \approx & H_{ee} & > & H_{SO} & \text{intermediate field} \\
4f^N & H_{ee} & > & H_{SO} & > & H_{LF} & \text{(a)} \\
H_{ee} & > & H_{SO} & \gg & H_{LF} & \text{(b)} \\
\end{array}
\]

\(a)\) strong field lanthanide system ; \(b)\) weak field lanthanide system

Table 1 gives approximate sizes of the corresponding energy splittings, including \(H_{ex}\) and \(H_{mag}\).

\(^1\) Localised electrons are presupposed.
Table 1 Effects acting on d and f electrons.

<table>
<thead>
<tr>
<th>Effect</th>
<th>System</th>
<th>Energy equivalent wavenumber/cm&lt;sup&gt;a)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-electron interaction $H_{ee}$</td>
<td>3d, 4d, 5d 4f, 5f</td>
<td>$3d &gt; 4d &gt; 5d \approx 10^4$&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ligand-field potential $H_{LF}$</td>
<td>3d, 4d, 5d 4f</td>
<td>$3d &lt; 4d &lt; 5d \approx 2 \times 10^4$&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Spin-orbit coupling $H_{SO}$</td>
<td>3d, 4d, 5d 4f, 5f</td>
<td>$3d &lt; 4d &lt; 5d \approx 10^3$&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Exchange interaction $H_{ex}$</td>
<td>nd 4f</td>
<td>$\leq 10^2$&lt;sup&gt;b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Exchange interaction $H_{ex}$</td>
<td>nd–4f</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Magnetic field $H_{mag}$</td>
<td></td>
<td>$\approx 0.5$ (1 T)</td>
</tr>
</tbody>
</table>

<sup>a)</sup> Conversion to other units, see Table 34 (Appendix).
<sup>b)</sup> Approximate value according to ref. [1].

Inspecting Table 1, two points are important for 4f ions: (i) $H_{ex}$ is at least two orders of magnitude smaller than $H_{LF}$ (and $H_{SO}$). (ii) $H_{mag}$ has to be chosen carefully on account of comparable magnitude of $H_{ex}$ and $H_{mag}$. Therefore, in order to detect $H_{ex}$, $H_{LF}$ should be modelled most exactly and $H_{mag}$ should be very weak.

1.3 Magnetic behaviour of Ln ions

The variation of $\chi_m$, $\mu$ (permanent magnetic moment corresponding with the Curie constant $C$), $\mu_{eff}$ (effective Bohr magneton number<sup>2)</sup>), $\chi_mT$, $M_m$ as a function of $T$ and $B_0$ serves to characterize the low-lying electronic states of the magnetic systems.

1.3.1 Ground multiplet thermally isolated ($\Delta E(J, J - 1) \gg k_B T$)

Neglecting $H_{LF}$, Hund’s formula eq. (1)

$$\mu \approx g_J \sqrt{J(J + 1)} \mu_B$$

(except 4f<sup>4</sup>, 4f<sup>5</sup>, 4f<sup>6</sup> systems) (1)

applies, where $J$ is the total angular momentum of the ground multiplet and $g_J$ the Landé factor

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

(2)

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

<sup>2)</sup> Note that the empirical number $\mu_{eff}$ has no connexion with the permanent moment $\mu$ except when Curie’s law is obeyed [2].
A graph showing the variation $\mu_{\text{eff}}$ vs. $T$ is recommended for 4f/5f systems\(^3\). According to Kramers’ rule [4], ions with an odd number of 4f electrons (half integral values of $\mu$) have always a degenerate ground state obeying the Curie law at low temperature (regardless the symmetry of $H_{\text{LF}}$, but presupposed that (i) solely the ligand field (LF) ground state is occupied and (ii) cooperative magnetic effects are absent). For an even number of f electrons, degenerate as well as singlet ground states can be found depending on the symmetry of $H_{\text{LF}}$. A singlet ground state produces temperature independent paramagnetism (TIP) at low temperature.

Going to 5f electron systems, $H_{\text{SO}}$ and $H_{\text{LF}}$ increase according to the larger effective nuclear charge and according to the fact that 5f electrons are more accessible for ligands. No simple approximation can be made. So, the only possibility to predict the magnetic behaviour for 5f ions are computational methods.

1.3.2 Ground multiplet thermally not isolated ($\Delta E(J, J - 1) \approx k_B T$)

General equation:  

$$\chi_m = \frac{\mu_0 N_A \mu_B^2}{3k_B T} \sum_{J=L-S}^{L+S} (2J + 1) \Lambda_J \exp \left\{ -\frac{\lambda_{L,S} J(J+1)}{2k_B T} \right\} \sum_{J=L-S}^{L+S} (2J + 1) \exp \left\{ -\frac{\lambda_{L,S} J(J+1)}{2k_B T} \right\}$$

where  

$$\Lambda_J = g_J^2 J(J+1) + 2(g_J - 1)(g_J - 2) \frac{k_B T}{\lambda_{L,S}}$$  and  

$$\lambda_{L,S} = \pm \frac{\zeta}{2S}$$

The $g_J$ values are given by eq. (2) (exception: $g_J = L + 2$ for $J = 0$). The term spin-orbit coupling parameter $\lambda_{L,S}$ is positive for ions with less than half-full subshell and negative for ions with more than half-full subshell.

Example 1.1 4f\(^6\) (Sm\(^{2+}\), Eu\(^{3+}\))

$$\chi_m = \mu_0 \frac{N_A \mu_B^2}{3k_B T} \mu_{\text{eff}}^2$$  where

$$\mu_{\text{eff}}^2 = Z^{-1} \left\{ 144 \frac{k_B T}{\zeta} + \frac{27}{2} - 9 \frac{k_B T}{\zeta} \right\} \exp \left( -\frac{\zeta}{6k_B T} \right)$$

$$+ \left( 135 \frac{k_B T}{\zeta} \right) \exp \left( -\frac{\zeta}{2k_B T} \right) + \left( 189 - 21 \frac{k_B T}{\zeta} \right) \exp \left( -\frac{\zeta}{k_B T} \right)$$

$$+ \left( 405 - 27 \frac{k_B T}{\zeta} \right) \exp \left( -\frac{5\zeta}{3k_B T} \right) + \left( \frac{1485}{2} - 33 \frac{k_B T}{\zeta} \right) \exp \left( -\frac{5\zeta}{2k_B T} \right)$$

$$+ \left( \frac{2457}{2} - 39 \frac{k_B T}{\zeta} \right) \exp \left( -\frac{7\zeta}{2k_B T} \right)$$

and

$$Z = \left\{ 1 + 3 \exp \left( -\frac{\zeta}{6k_B T} \right) + 5 \exp \left( -\frac{\zeta}{2k_B T} \right) + 7 \exp \left( -\frac{\zeta}{k_B T} \right) \right\}$$

$$+ 9 \exp \left( -\frac{5\zeta}{3k_B T} \right) + 11 \exp \left( -\frac{5\zeta}{2k_B T} \right) + 13 \exp \left( -\frac{7\zeta}{2k_B T} \right) \right\}$$

\(^3\) We recommend this plot or alternatively $\mu_{\text{eff}}^2$ vs. $T$ instead of the $\chi_m$ vs. $T$ plot for two reasons: (i) The number $\mu_{\text{eff}}$ has the same numerical value in the SI and CGS-emu system, (ii) $\mu_{\text{eff}}$ is easily compared with the lanthanide’s corresponding free-ion value $\mu_{\text{eff}} = g_J \sqrt{J(J+1)}$ [5].
Eq. (4) is calculated with \( g_J = \frac{3}{2} \) for the multiplets \( J = 1, 2, 3, 4, 5, 6 \), \( g_J = 5 \) for \( J = 0 \), and \( \lambda_{LS} = \zeta / 6 \).

**Table 2**: Lanthanide ions: term symbol (ground state), one-electron spin-orbit coupling parameter \( \zeta_{4f} \) [cm\(^{-1}\)], \( g_J \), \( g_J J \), \( g_J[J(J+1)]^{1/2} \) and \( \mu_{\text{eff}}^{\text{exp}}(295 \text{K}) \) [7]

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

\(^a\) The relation between \( \zeta_{4f} \) and \( \lambda_{LS} \) 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.

\(^b\) Definition: \( \chi_m = \mu_0 N_A \mu_B^2 \mu_{\text{eff}}^2 /(3 k_B T) \).

\(^c\) Diamagnetic

\(^d\) Observed for Nd\(^{2+}\) compounds.

**Problems**

1. Verify the Russell-Saunders ground multiplets for Nd\(^{2+}\) and Er\(^{3+}\) given in Table 2.

2. Evaluate the susceptibility equation for a free \( p^1 \) system perturbed by spin-orbit coupling. (Hint: Apply eq. (3). Note that for the single-electron system \( \lambda_{LS} \equiv \zeta \). Solutions are given in section 5.)
2 Theory of free lanthanide ions

2.1 Functions

Schrödinger equation (spin ignored):

\[
\left[ -\frac{\hbar^2}{2m_e} \nabla^2 - e\hat{V}(r) \right] \psi(r) = E\psi(r)
\]  

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

\[
\begin{align*}
x &= r \cdot \sin \theta \cdot \cos \phi \\
y &= r \cdot \sin \theta \cdot \sin \phi \\
z &= r \cdot \cos \theta \\
x^2 &= x^2 + y^2 + z^2 \\
\cos \theta &= z/r \\
tan \phi &= y/x
\end{align*}
\]  

The functions \(Y_{m_l}^l(\theta, \phi)\) are spherical harmonics specified by the quantum numbers \(l\) and \(m_l\) (Table 3). Real functions (Table 4) are gained by linear combinations

\[
\begin{align*}
\frac{1}{\sqrt{2}} [-\psi_{n,l,m_l} + \psi_{n,l,-m_l}] &= \frac{1}{\sqrt{\pi}} R_{n,l}(r) \Theta_{m_l}^l(\theta) \cos m_l \phi & m_l \text{ odd} \\
\frac{1}{i\sqrt{2}} [-\psi_{n,l,m_l} - \psi_{n,l,-m_l}] &= \frac{1}{\sqrt{\pi}} R_{n,l}(r) \Theta_{m_l}^l(\theta) \sin m_l \phi & m_l \text{ odd} \\
\frac{1}{\sqrt{2}} [\psi_{n,l,m_l} + \psi_{n,l,-m_l}] &= \frac{1}{\sqrt{\pi}} R_{n,l}(r) \Theta_{m_l}^l(\theta) \cos m_l \phi & m_l \text{ even} \\
\frac{1}{i\sqrt{2}} [\psi_{n,l,m_l} - \psi_{n,l,-m_l}] &= \frac{1}{\sqrt{\pi}} R_{n,l}(r) \Theta_{m_l}^l(\theta) \sin m_l \phi & m_l \text{ even}
\end{align*}
\]  

For a complete description of the wave function, the spin has to be taken into consideration. Ignoring spin-orbit coupling, the total function (spin orbital) reads

\[
\psi(r, \theta, \phi; \sigma) = \psi(r, \theta, \phi) \psi(\sigma) \quad \text{where} \quad \sigma = \pm \frac{1}{2}.
\]
Table 3: Spherical harmonics for $l = 0, 1, 2, 3$

<table>
<thead>
<tr>
<th>$l$</th>
<th>$m_l$</th>
<th>$Y_{ml}^{l}(\theta, \phi)^a$</th>
<th>$Y_{ml}^{l}(x, y, z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$(\frac{1}{4\pi})^{1/2}$</td>
<td>$(\frac{1}{4\pi})^{1/2}$</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>$(\frac{3}{8\pi})^{1/2} \sin \theta e^{\pm i\phi}$</td>
<td>$(\frac{3}{8\pi})^{1/2} x \pm iy$</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>$(\frac{5}{16\pi})^{1/2} (3 \cos^2 \theta - 1)$</td>
<td>$(\frac{5}{16\pi})^{1/2} \frac{3z^2 - r^2}{r^2}$</td>
</tr>
<tr>
<td></td>
<td>±2</td>
<td>$(\frac{15}{32\pi})^{1/2} \cos \theta \sin \theta e^{\pm i\phi}$</td>
<td>$(\frac{15}{32\pi})^{1/2} \frac{(x \pm iy)^2}{r^2}$</td>
</tr>
<tr>
<td>3</td>
<td>±1</td>
<td>$(\frac{7}{16\pi})^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$</td>
<td>$(\frac{7}{16\pi})^{1/2} \frac{5z^2 - 3r^2}{r^3}$</td>
</tr>
<tr>
<td></td>
<td>±2</td>
<td>$(\frac{21}{64\pi})^{1/2} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$</td>
<td>$(\frac{21}{64\pi})^{1/2} \frac{(x \pm iy)(5z^2 - r^2)}{r^3}$</td>
</tr>
<tr>
<td></td>
<td>±3</td>
<td>$(\frac{105}{32\pi})^{1/2} \cos \theta \sin^2 \theta e^{\pm i2\phi}$</td>
<td>$(\frac{105}{32\pi})^{1/2} \frac{z(x \pm iy)^2}{r^3}$</td>
</tr>
<tr>
<td></td>
<td>±3</td>
<td>$(\frac{35}{64\pi})^{1/2} \sin^3 \theta e^{\pm i3\phi}$</td>
<td>$(\frac{35}{64\pi})^{1/2} \frac{(x \pm iy)^3}{r^3}$</td>
</tr>
<tr>
<td>4</td>
<td>±1</td>
<td>$(\frac{9}{256\pi})^{1/2} (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$</td>
<td>$(\frac{9}{256\pi})^{1/2} \frac{(35z^4 - 30z^2r^2 + 3r^4)}{r^4}$</td>
</tr>
<tr>
<td></td>
<td>±2</td>
<td>$(\frac{45}{128\pi})^{1/2} \sin \theta (7 \cos^3 \theta - 3 \cos \theta) e^{\pm i\phi}$</td>
<td>$(\frac{45}{128\pi})^{1/2} \frac{(x \pm iy)(7z^3 - 3zr^2)}{r^4}$</td>
</tr>
<tr>
<td></td>
<td>±3</td>
<td>$(\frac{45}{128\pi})^{1/2} \sin^2 \theta (7 \cos^2 \theta - 1) e^{\pm i2\phi}$</td>
<td>$(\frac{45}{128\pi})^{1/2} \frac{(x \pm iy)^2(7z^2 - r^2)}{r^4}$</td>
</tr>
<tr>
<td></td>
<td>±3</td>
<td>$(\frac{315}{64\pi})^{1/2} \sin^3 \theta \cos \theta e^{\pm i3\phi}$</td>
<td>$(\frac{315}{64\pi})^{1/2} \frac{z(x \pm iy)^3}{r^4}$</td>
</tr>
<tr>
<td></td>
<td>±4</td>
<td>$(\frac{315}{512\pi})^{1/2} \sin^4 \theta e^{\pm i4\phi}$</td>
<td>$(\frac{315}{512\pi})^{1/2} \frac{(x \pm iy)^4}{r^4}$</td>
</tr>
</tbody>
</table>

$a$) Phase factors correspond to the CONDON-SHORTLEY convention: $-1$ for odd positive $m_l$ and $+1$ otherwise.
Table 4: Real orthonormal linear combinations of the spherical harmonics $Y_{lm}^l(\theta, \phi)$ for $l = 1, 2, 3$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>function</th>
<th>designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \left( \frac{3}{4\pi} \right)^{1/2} \cos \theta )</td>
<td>( \left( \frac{3}{4\pi} \right)^{1/2} \frac{z}{r} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{3}{4\pi} \right)^{1/2} \sin \theta \cos \phi )</td>
<td>( \left( \frac{3}{4\pi} \right)^{1/2} \frac{x}{r} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{3}{4\pi} \right)^{1/2} \sin \theta \sin \phi )</td>
<td>( \left( \frac{3}{4\pi} \right)^{1/2} \frac{y}{r} )</td>
</tr>
<tr>
<td>2</td>
<td>( \left( \frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1) )</td>
<td>( \left( \frac{5}{16\pi} \right)^{1/2} \frac{3z^2 - r^2}{r^2} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{15}{4\pi} \right)^{1/2} \cos \theta \sin \theta \cos \phi )</td>
<td>( \left( \frac{15}{4\pi} \right)^{1/2} \frac{xz}{r^2} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{15}{4\pi} \right)^{1/2} \sin \theta \sin \theta \sin \phi )</td>
<td>( \left( \frac{15}{4\pi} \right)^{1/2} \frac{yz}{r^2} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{15}{16\pi} \right)^{1/2} \sin^2 \theta \cos 2\phi )</td>
<td>( \left( \frac{15}{16\pi} \right)^{1/2} \frac{x^2 - y^2}{r^2} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{15}{16\pi} \right)^{1/2} \sin^2 \theta \sin 2\phi )</td>
<td>( \left( \frac{15}{4\pi} \right)^{1/2} \frac{xy}{r^2} )</td>
</tr>
<tr>
<td>3</td>
<td>( \left( \frac{7}{16\pi} \right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta) )</td>
<td>( \left( \frac{7}{16\pi} \right)^{1/2} \frac{z(5z^2 - 3r^2)}{r^3} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{21}{32\pi} \right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) \cos \phi )</td>
<td>( \left( \frac{21}{32\pi} \right)^{1/2} \frac{x(5z^2 - r^2)}{r^3} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{21}{32\pi} \right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) \sin \phi )</td>
<td>( \left( \frac{21}{32\pi} \right)^{1/2} \frac{y(5z^2 - r^2)}{r^3} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{105}{16\pi} \right)^{1/2} \cos \theta \sin^2 \theta \sin 2\phi )</td>
<td>( \left( \frac{105}{4\pi} \right)^{1/2} \frac{xyz}{r^3} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{105}{16\pi} \right)^{1/2} \cos \theta \sin^2 \theta \cos 2\phi )</td>
<td>( \left( \frac{105}{16\pi} \right)^{1/2} \frac{z(x^2 - y^2)}{r^3} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{35}{32\pi} \right)^{1/2} \sin^3 \theta \cos 3\phi )</td>
<td>( \left( \frac{35}{32\pi} \right)^{1/2} \frac{x(x^2 - 3y^2)}{r^3} )</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{35}{32\pi} \right)^{1/2} \sin^3 \theta \sin 3\phi )</td>
<td>( \left( \frac{35}{32\pi} \right)^{1/2} \frac{y(3x^2 - y^2)}{r^3} )</td>
</tr>
</tbody>
</table>
2.2 Angular momenta

2.2.1 Orbital angular momentum

Classical definition of the angular momentum $\mathbf{l}$ (Fig. 2):

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}. \quad \text{(10)}$$

*Fig. 2: Definition of the angular momentum*

$$\mathbf{l} = l_x \mathbf{i} + l_y \mathbf{j} + l_z \mathbf{k}$$

Length of the angular momentum vector:

$$|\mathbf{l}|^2 = l_x^2 + l_y^2 + l_z^2. \quad \text{(12)}$$

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

$$q \rightarrow \hat{q} = q \times \quad \text{p}_q \rightarrow \hat{p}_q = \frac{\hbar}{i} \frac{\partial}{\partial q} \quad (q = x, y, z; \quad i = \sqrt{-1})$$

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

$$\hat{l}_x = \frac{\hbar}{i} \left( \hat{y} \frac{\partial}{\partial z} - \hat{z} \frac{\partial}{\partial y} \right); \quad \hat{l}_y = \frac{\hbar}{i} \left( \hat{z} \frac{\partial}{\partial x} - \hat{x} \frac{\partial}{\partial z} \right); \quad \hat{l}_z = \frac{\hbar}{i} \left( \hat{x} \frac{\partial}{\partial y} - \hat{y} \frac{\partial}{\partial x} \right) \quad \text{(14)}$$

Commutation relations

$$[\hat{l}_x, \hat{l}_y] = i \hbar \hat{l}_z; \quad [\hat{l}_y, \hat{l}_z] = i \hbar \hat{l}_x; \quad [\hat{l}_z, \hat{l}_x] = i \hbar \hat{l}_y. \quad \text{(15)}$$

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

$$\hat{l}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad \text{(16)}$$

$\hat{l}_z$ acts on the $\phi$ depending part of the atomic orbitals (Table 3):

$$\hat{l}_z | l m_l \rangle = l_z | l m_l \rangle = m_l \hbar | l m_l \rangle \quad \text{Dirac notation}$$

$$\langle l m_l | \hat{l}_z | l m_l \rangle = m_l \hbar \langle l m_l | l m_l \rangle_1$$
generally \( \hat{H} \Psi = E \Psi \) (\( \Psi \) normalised eigenfunction of \( \hat{H} \))

\[
\int \Psi^* \hat{H} \Psi \, d\tau = E \int \Psi^* \Psi \, d\tau = E
\]

\[
\int \Psi^* \hat{H} \Psi \, d\tau \equiv \langle \Psi | \hat{H} | \Psi \rangle \quad \text{matrix element (Dirac notation)}
\]

Application of \( \hat{l}_z \):

\[
\hat{l}_z \left| \begin{array}{c} 2 \ 2 \end{array} \rightangle = R_{n,2}(r) \frac{\hbar}{i} \left\{ \frac{\partial}{\partial \phi} Y_2^n(\theta, \phi) \right\}
\]

\[
= R_{n,2}(r) \frac{\hbar}{i} \frac{\partial}{\partial \phi} \left[ \left( \frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{i2\phi} \right]
\]

\[
= R_{n,2}(r) \frac{\hbar}{i} \left( \frac{15}{32\pi} \right)^{1/2} \sin^2 \theta \frac{\partial e^{i2\phi}}{\partial \phi}
\]

\[
= R_{n,2}(r)i2 \frac{\hbar}{i} \left( \frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{i2\phi} = 2\hbar \left| \begin{array}{c} 2 \ 2 \end{array} \rightangle
\]

\[
\hat{l}^2 \mid l m_t \rangle = l(l+1)\hbar^2 \mid l m_t \rangle
\]

Shift operators:

\( \hat{l}_+ = \hat{l}_x + i\hat{l}_y; \quad \hat{l}_- = \hat{l}_x - i\hat{l}_y. \)

Reverse operations:

\( \hat{l}_x = \frac{1}{2}(\hat{l}_+ + \hat{l}_-); \quad \hat{l}_y = \frac{1}{2i}(\hat{l}_+ - \hat{l}_-). \)

\[
\begin{align*}
\hat{l}_z \mid l m_t \rangle &= m_t \hbar \mid l m_t \rangle \\
\hat{l}^2 \mid l m_t \rangle &= l(l+1)\hbar^2 \mid l m_t \rangle \\
\hat{l}_\pm \mid l m_t \rangle &= \sqrt{l(l+1) - m_t(m_t \pm 1)} \hbar \mid l m_t \pm 1 \rangle.
\end{align*}
\]

**Fig. 3:** Specified orientation of \( \mathbf{l} \) \( (l = 2) \) with regard to the component \( l_z \) while \( l_x \) and \( l_y \) are unspecified
2.2.2 Spin

Spin orbital of a one-electron system:

\[ \psi(r) \psi(\sigma) = \psi_{n,l,m}(r, \theta, \phi) \psi(\sigma) = R_{n,l}(r) Y_{m_l}^l(\theta, \phi) \psi(\sigma) \]

atomic orbital

Spin function: \( \psi(\sigma) \equiv |s m_s\rangle \)

\[
\begin{align*}
\mathbf{S}^2 | s m_s \rangle &= s(s+1) \hbar^2 | s m_s \rangle \quad \text{with} \quad s = \frac{1}{2} \\
\mathbf{S}_z | s m_s \rangle &= m_s \hbar | s m_s \rangle \quad \text{with} \quad m_s = \pm \frac{1}{2} \\
\mathbf{S}_\pm | s m_s \rangle &= \sqrt{s(s+1) - m_s(m_s \pm 1)} \hbar | s m_s \pm 1 \rangle
\end{align*}
\]

where \( \mathbf{S}^2 = \mathbf{S}_x^2 + \mathbf{S}_y^2 + \mathbf{S}_z^2; \quad \mathbf{S}_+ = \mathbf{S}_x + i\mathbf{S}_y; \quad \mathbf{S}_- = \mathbf{S}_x - i\mathbf{S}_y \)

\[ \mathbf{S}_x = \frac{1}{2} (\mathbf{S}_+ + \mathbf{S}_-); \quad \mathbf{S}_y = \frac{i}{2} (\mathbf{S}_+ - \mathbf{S}_-) \]

Problems

3. Use the spherical harmonics in Table 3 and construct the real functions \( d_{x^2-y^2} \) and \( d_{xy} \) with the help of eqs. (8). Verify the results with the data given in Table 4.

2.3 Quantum-mechanical procedures

2.3.1 Operators

Postulate 1. The state of a system is fully described by the wavefunction \( \Psi(r_1, r_2, \ldots, t) \).

Postulate 2. Observables are represented by operators chosen to satisfy the commutation relation

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

Example 2.1 Verification of the commutation relation

\[ \hat{x} = x \times \quad \text{and} \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \]

\[
\begin{align*}
\hat{x} \hat{p}_x \Psi &= \frac{\hbar}{i} \frac{d\Psi}{dx} \\
\hat{p}_x \hat{x} \Psi &= \frac{\hbar}{i} \frac{d(x\Psi)}{dx} = \frac{\hbar}{i} \left( \Psi + x \frac{d\Psi}{dx} \right) \\
(\hat{x} \hat{p}_x - \hat{p}_x \hat{x}) \Psi &= -\frac{\hbar}{i} \Psi = i\hbar \Psi
\end{align*}
\]
### Tab. 5: Classical and quantum-mechanical forms of $E_{\text{kin}}$ and $E_{\text{pot}}$

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Classical</th>
<th>Quantum-Mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{kin}}$</td>
<td>$\frac{m_e v_x^2}{2} = \frac{p_x^2}{2m_e}$</td>
<td>$\frac{\hat{p}_x^2}{2m_e} = \frac{1}{2m_e} \left( \frac{\hbar}{i} \frac{d}{dx} \right)^2 = -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2}$</td>
</tr>
<tr>
<td></td>
<td>$\frac{p^2}{2m_e}$</td>
<td>$-\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$</td>
</tr>
<tr>
<td>$E_{\text{pot}}$</td>
<td>$-eV(x)$</td>
<td>$-e\hat{V}(x) = -eV(x)$</td>
</tr>
<tr>
<td></td>
<td>$-eV(r)$</td>
<td>$-e\hat{V}(r) = -eV(r)$</td>
</tr>
</tbody>
</table>

- $^a$ Dimension.
- $^b$ $\nabla$ is the Nabla operator.
- $^c$ Valid for one electron with charge $-e$ in the potential $V$.

#### 2.3.2 Perturbation theory

1. **Non-degenerate states**

   $\hat{H}(0) \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ \quad unperturbed system

   Hamilton operator of the perturbed system:

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

   Schrödinger equation of the perturbed system:

   $\hat{H} \psi_n = E_n \psi_n$; \quad find $E_n, \psi_n$ \quad (24)

   Series expansion of $\psi_n$ und $E_n$:

   $\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots$ \quad (25)

   $E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$ \quad (26)

   Insert the series into eq. (24):

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

   $(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots),$

   Ordering of the terms with regard to powers of $\lambda$:

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

   $E_n^{(0)} \psi_n^{(0)} + \lambda(E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}) +$

   $\lambda^2(E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(0)} \psi_n^{(2)}) + \ldots$
\begin{align}
\lambda^0 \quad \hat{H}(0)\psi_n^{(0)} &= E_n^{(0)}\psi_n^{(0)} \\
\lambda^1 \quad (\hat{H}(0) - E_n^{(0)})\psi_n^{(1)} &= (E_n^{(1)} - \hat{H}(1))\psi_n^{(0)} \\
\lambda^2 \quad (\hat{H}(0) - E_n^{(0)})\psi_n^{(2)} &= E_n^{(2)}\psi_n^{(0)} + (E_n^{(1)} - \hat{H}(1))\psi_n^{(1)} \\
&\vdots
\end{align}

The first-order correction to the energy \( E_n^{(1)} \)
(premultiply both sides of eq. (28) with \( \psi_n^{(0)*} \) and integrate)
\[
\int_0^\infty \psi_n^{(0)*}\hat{H}(0)\psi_n^{(1)} d\tau - \int_0^\infty \psi_n^{(0)*}\psi_n^{(1)} d\tau = E_n^{(1)} - \int_0^\infty \psi_n^{(0)*}\hat{H}(1)\psi_n^{(0)} d\tau
\]

\[E_n^{(1)} = \langle n|\hat{H}^{(1)}|n \rangle\] (30)

The first-order correction to the wavefunction:
\[
\psi_n^{(1)} = -\sum_{m \neq n} \frac{\langle m|\hat{H}^{(1)}|n \rangle}{E_m^{(0)} - E_n^{(0)}} \psi_m^{(0)}
\]
(31)

The second-order correction to the energy:
\[
E_n^{(2)} = -\sum_{m \neq n} \frac{|\langle m|\hat{H}^{(1)}|n \rangle|^2}{E_m^{(0)} - E_n^{(0)}}
\] (32)

\begin{figure}
\centering
\includegraphics{fig4}
\caption{Illustration of the possible effects of a perturbation on two non-degenerate levels; (a) 0\(^{th}\), (b) 1\(^{st}\), (c) 2\(^{nd}\) order}
\end{figure}
2. Degenerate states

Eq. (30) – (32) apply also in this case; additionally: determination of the correct zeroth-order wavefunctions (see Fig. 5)

Example: doubly degenerate pair of states

\[
\hat{H}^{(0)} \Psi^{(0)}_{n,i} = E^{(0)}_n \Psi^{(0)}_{n,i} \quad (i = 1, 2)
\]  

(33)

\[
\Psi^{(0)}_n = u_1 \Psi^{(0)}_{n,1} + u_2 \Psi^{(0)}_{n,2}
\]

(34)

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. (34) in eq. (25); eq. (28) now reads:

\[
(\hat{H}^{(0)} - E^{(0)}_n) \Psi^{(1)}_n = (E^{(1)}_n - \hat{H}^{(1)}) (u_1 \Psi^{(0)}_{n,1} + u_2 \Psi^{(0)}_{n,2})
\]

(35)

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

\[
u_1 (H_{11} - E^{(1)}_n) + u_2 H_{12} = 0
\]

\[
u_1 H_{21} + u_2 (H_{22} - E^{(1)}_n) = 0
\]

where \( H_{ij} = \int \Psi^{(0)*}_{n,i} \hat{H}^{(1)} \Psi^{(0)}_{n,j} d\tau = \langle i | \hat{H}^{(1)} | j \rangle \)

To find the non-trivial solutions of this pair of equations, the determinant of the coefficients of the constants \( u_1 \) and \( u_2 \) must disappear:

\[
\begin{vmatrix}
H_{11} - E^{(1)}_n & H_{12} \\
H_{21} & H_{22} - E^{(1)}_n
\end{vmatrix} = 0;
\]

\( H_{11}, H_{22} \) : diagonal elements

\( H_{12}, H_{21} \) : off-diagonal elements

(36)

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

\[
u_1(1,2) (H_{11} - E^{(1)}_{n(1,2)}) + u_2(1,2) H_{12} = 0;
\]

\[
x_{(1,2)} = \frac{u_1(1,2)}{u_2(1,2)} = -\frac{H_{12}}{H_{11} - E^{(1)}_{n(1,2)}}
\]

Normalisation:

\[
x_{(1,2)}^2 u_{1(1,2)}^2 + u_{2(1,2)}^2 = 1 \quad \Rightarrow \quad \begin{cases} 
    u_{2(1,2)} = \frac{1}{\sqrt{x_{(1,2)}^2 + 1}} \\
    u_{1(1,2)} = x_{(1,2)} u_{2(1,2)} = \frac{x_{(1,2)}}{\sqrt{x_{(1,2)}^2 + 1}}
\end{cases}
\]

Correct zeroth-order wavefunctions 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. 5: 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

Alternative procedure to solve $2 \times 2$ determinants (cf. [11], p. 119):

General solution for $2 \times 2$ determinants:

$$
\begin{vmatrix}
H_{11} - E & H_{12} \\
H_{12} & H_{22} - E
\end{vmatrix} = 0.
\quad \tan 2\alpha = \frac{2H_{12}}{(H_{11} - H_{22})}
$$

$$
E = \begin{cases}
H_{11} - H_{12} \cot \alpha; & \Psi_1 = \sin \alpha \psi_1 - \cos \alpha \psi_2 \\
H_{22} + H_{12} \cot \alpha; & \Psi_2 = \cos \alpha \psi_1 + \sin \alpha \psi_2
\end{cases}
$$

$$
H_{ij} = \langle \psi_i | \hat{H}^{(1)} | \psi_j \rangle
$$

(37)
2.4 Applications

2.4.1 Spin-orbit coupling (p^1, f^1, f^{13})

Example 2.2 p^1 system

\[ \hat{H}_{\text{SO}} = \xi(r) \hat{l} \cdot \hat{s} \quad \text{where} \quad \xi(r) = -\frac{e}{2m_e^2c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r}. \] (38)

p^1 system: \( l = 1, s = \frac{1}{2}, j_1 = l - s = \frac{1}{2} \) and \( j_2 = l + s = \frac{3}{2} \) (see Figs. 6 and 7, Table 6)

\[ \begin{align*}
\text{spin-orbit coupling} & \quad 0 & 1 \quad \frac{1}{2} \xi \\
E^{(0)} (6) & \quad 0 & \frac{1}{2} \xi \\
E^{(0)} (4) & \quad 0 & 1 \\
\text{off} & \quad \text{on} & -\xi
\end{align*} \]

**Fig. 6:** Splitting of the p^1 levels by spin-orbit interaction (\( \xi \): one-electron spin-orbit coupling constant)

Unperturbed states sixfold degenerate

\[ \hat{H}^{(0)} \psi_i^{(0)} = E^{(0)} \psi_i^{(0)} \quad (i = 1, 2, \ldots, 6). \]

Eq. (35) reads in this case:

\[ (\hat{H}^{(0)} - E^{(0)}) \psi^{(1)} = (E^{(1)} - \hat{H}^{(1)}) (u_1 \psi_1^{(0)} + \ldots + u_6 \psi_6^{(0)}). \] (39)

Premultiplication with \( \psi_1^{(0)\ast} \) and integration result in:

\[ \int_0 \psi_1^{(0)\ast} (\hat{H}^{(0)} - E^{(0)}) \psi^{(1)} d\tau = \int \psi_1^{(0)\ast} (E^{(1)} - \hat{H}^{(1)}) (u_1 \psi_1^{(0)} + \ldots + u_6 \psi_6^{(0)}) d\tau \]

\[ 0 = u_1 E^{(1)} \int \psi_1^{(0)\ast} \psi_1^{(0)} d\tau + \ldots + u_6 E^{(1)} \int \psi_1^{(0)\ast} \psi_6^{(0)} d\tau \\
- u_1 \int \psi_1^{(0)\ast} \hat{H}^{(1)} \psi_1^{(0)} d\tau - \ldots - u_6 \int \psi_1^{(0)\ast} \hat{H}^{(1)} \psi_6^{(0)} d\tau. \] (40)
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{align}
0 &= u_{1}(H_{11} - E^{(1)}) + u_{2}H_{12} + \cdots + u_{6}H_{61} \\
0 &= u_{1}H_{21} + u_{2}(H_{22} - E^{(1)}) + \cdots + u_{6}H_{62} \\
&\vdots \\
0 &= u_{1}H_{61} + u_{2}H_{62} + \cdots + u_{6}(H_{66} - E^{(1)})
\end{align} \tag{41}

Non-trivial solutions for the coefficients of $u_{1}, u_{2}, \ldots, u_{6}$:

Calculation of the integrals $H_{ij}$

\[
\int_{0}^{\infty} R_{n,l}(r) \xi(r) R_{n,l}(r) r^{2} dr \times \int_{0}^{\pi} \int_{-1/2}^{1/2} (Y_{m}^{m_{l}}(\theta, \phi) \psi_{m_{l}}(\sigma))^{*} \hat{\mathbf{s}} \cdot \mathbf{s} (Y_{l}^{m_{l}}(\theta, \phi) \psi_{m_{l}}(\sigma)) \sin \theta d\theta d\phi d\sigma.
\]

\[
hc \zeta_{n,l} = \hbar^{2} \int_{0}^{\infty} R_{n,l}(r) \xi(r) R_{n,l}(r) r^{2} dr.
\]

$\zeta_{n,l}$: one-electron spin-orbit coupling constant

basis in Dirac notation: $| m_{l} m_{s} \rangle$

\[
| 1 \frac{1}{2} \rangle | 0 \frac{1}{2} \rangle | -1 \frac{1}{2} \rangle | 1 - \frac{1}{2} \rangle | 0 - \frac{1}{2} \rangle | -1 - \frac{1}{2} \rangle.
\]

Integral eq. (43) has the short form

\[
\frac{hc \zeta_{n,l}}{\hbar^{2}} \langle m_{l} m_{s} | \hat{\mathbf{s}} \cdot \mathbf{s} | m'_{l} m'_{s} \rangle.
\]

To determine the 36 matrix elements of the spin-orbit coupling operator $\hat{\mathbf{s}} \cdot \mathbf{s} = \hat{\mathbf{s}}_{x} + \hat{\mathbf{s}}_{y} + \hat{\mathbf{s}}_{z}$, replace the $x$ and $y$ components by the step operators (see eq. (19,21)):

\[
\hat{\mathbf{s}} \cdot \mathbf{s} = \hat{\mathbf{s}}_{z} + \frac{1}{2} (\hat{\mathbf{s}}_{+} + \hat{\mathbf{s}}_{-}) + \frac{1}{2} (\hat{\mathbf{s}}_{+} - \hat{\mathbf{s}}_{-}) \frac{1}{2} (\hat{\mathbf{s}}_{+} + \hat{\mathbf{s}}_{-})
\]

\[
= \hat{\mathbf{s}}_{z} + \frac{1}{2} \hat{\mathbf{s}}_{+} + \hat{\mathbf{s}}_{-} + \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-} + \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-} + \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-} + \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-}
\]

\[
= \hat{\mathbf{s}}_{z} + \hat{\mathbf{s}}_{+} + \hat{\mathbf{s}}_{-} + \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-}
\]

The general matrix element (46) is

\[
\langle m_{l} m_{s} | \hat{\mathbf{s}} \cdot \mathbf{s} | m'_{l} m'_{s} \rangle = \langle m_{l} m_{s} | \hat{\mathbf{s}}_{z} + \frac{1}{2} (\hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-} + \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-}) | m'_{l} m'_{s} \rangle
\]

\[
= \langle m_{l} m_{s} | \hat{\mathbf{s}}_{z} | m'_{l} m'_{s} \rangle \\
+ \frac{1}{2} \langle m_{l} m_{s} | \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-} | m'_{l} m'_{s} \rangle \\
+ \frac{1}{2} \langle m_{l} m_{s} | \hat{\mathbf{s}}_{+} \hat{\mathbf{s}}_{-} | m'_{l} m'_{s} \rangle.
\]

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

(ii) The result of (i) is then premultiplied by \( \langle m | \) giving \( \langle m | a |n\rangle \).

(iii) Since \( a \) is a constant we have \( \langle m | |n\rangle = a \langle m | |n\rangle \) and we are thus left with the task of evaluating \( \langle m | |n\rangle \). Provided \( |m\rangle \) and \( |n\rangle \) are orthonormalised, \( \langle m | |n\rangle = 1 \) when \( m = n \) but is zero otherwise.

On account of orthonormalised states \( \langle m_t m_s | m'_t m'_s \rangle = \delta_{m_t,m'_t} \delta_{m_s,m'_s} \),

\[ (49) \]

the integral is not zero when \( m_t = m'_t \) and \( m_s = m'_s \). The wavefunctions are eigenfunctions of \( \hat{l}_z \) and \( \hat{s}_z \), so that the application of the operator products in eq. (48) on the wavefunction on its right-hand side yields:

\[
\begin{align*}
\langle \hat{l}_z \hat{s}_z | m_t m_s \rangle &= m_t m_s \hbar^2 | m_t m_s \rangle \\
\langle \hat{l}_+ \hat{s}_- | m_t m_s \rangle &= \sqrt{l(l+1) - m_t(m_t+1)} \sqrt{s(s+1) - m_s(m_s-1)} \hbar^2 | m_t + 1 m_s - 1 \rangle \\
\langle \hat{l}_- \hat{s}_+ | m_t m_s \rangle &= \sqrt{l(l+1) - m_t(m_t-1)} \sqrt{s(s+1) - m_s(m_s+1)} \hbar^2 | m_t - 1 m_s + 1 \rangle
\end{align*}
\]

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

\[
\langle m_t m_s | \hat{l}_+ \hat{s}_- | m_t - 1 m_s + 1 \rangle \quad \langle m_t m_s | \hat{l}_- \hat{s}_+ | m_t + 1 m_s - 1 \rangle
\]

Matrix elements (46) which may contribute are restricted to the condition \( m_t + m_s = m'_t + m'_s \)

\[ (50) \]

The non-zero matrix elements are:

\[
\begin{align*}
\langle 1 \frac{1}{2} | \hat{l}_+ \hat{s}_- | 0 \frac{1}{2} \rangle &= 0 \frac{1}{2} | \hat{l}_+ \hat{s}_- | -1 \frac{1}{2} \\
\langle 0 \frac{1}{2} | \hat{l}_- \hat{s}_+ | 1 - \frac{1}{2} \rangle &= -1 \frac{1}{2} | \hat{l}_- \hat{s}_+ | 0 - \frac{1}{2}
\end{align*}
\]

\[ (51) \]

<table>
<thead>
<tr>
<th>( m_t m_s )</th>
<th>( 1 \frac{1}{2} )</th>
<th>( 1 - \frac{1}{2} )</th>
<th>( 0 \frac{1}{2} )</th>
<th>( 0 - \frac{1}{2} )</th>
<th>( -1 \frac{1}{2} )</th>
<th>( -1 - \frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle 1 \frac{1}{2}</td>
<td>)</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
<td>( \sqrt{\frac{1}{2}} \zeta )</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
</tr>
<tr>
<td>( \langle 1 - \frac{1}{2}</td>
<td>)</td>
<td>( \sqrt{\frac{1}{2}} \zeta )</td>
<td>( 0 )</td>
<td>( \sqrt{\frac{1}{2}} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
<td>( \frac{1}{2} \zeta )</td>
</tr>
<tr>
<td>( \langle 0 \frac{1}{2}</td>
<td>)</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( \sqrt{\frac{1}{2}} \zeta )</td>
<td>( 0 )</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
</tr>
<tr>
<td>( \langle 0 - \frac{1}{2}</td>
<td>)</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( 0 )</td>
<td>( 0 )</td>
<td>( \frac{1}{2} \zeta )</td>
</tr>
<tr>
<td>( \langle -1 \frac{1}{2}</td>
<td>)</td>
<td>( -\frac{1}{2} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( \langle -1 - \frac{1}{2}</td>
<td>)</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
<td>( -\frac{1}{2} \zeta )</td>
<td>( \frac{1}{2} \zeta )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>
\[ H_{11} = \frac{\zeta}{\hbar^2} \langle 1 \frac{1}{2} | \hat{\sigma}_z | 1 \frac{1}{2} \rangle = \zeta \cdot 1 \frac{1}{2} \langle 1 \frac{1}{2} | 1 \frac{1}{2} \rangle = \frac{1}{2} \zeta \]
\[ H_{22} = \frac{\zeta}{\hbar^2} \langle 1 -\frac{1}{2} | \hat{\sigma}_z | 1 -\frac{1}{2} \rangle = \zeta \cdot 1 \langle -\frac{1}{2} \rangle = -\frac{1}{2} \zeta \]
\[ H_{33} = \frac{\zeta}{\hbar^2} \langle 0 \frac{1}{2} | \hat{\sigma}_z | 0 \frac{1}{2} \rangle = \zeta \cdot 0 \cdot \frac{1}{2} = 0 \]
\[ H_{44} = \frac{\zeta}{\hbar^2} \langle 0 -\frac{1}{2} | \hat{\sigma}_z | 0 -\frac{1}{2} \rangle = \zeta \cdot 0 \cdot (-\frac{1}{2}) = 0 \]
\[ H_{55} = \frac{\zeta}{\hbar^2} \langle -1 \frac{1}{2} | \hat{\sigma}_z | -1 \frac{1}{2} \rangle = \zeta \cdot (-1) \cdot \frac{1}{2} = -\frac{1}{2} \zeta \]
\[ H_{66} = \frac{\zeta}{\hbar^2} \langle -1 -\frac{1}{2} | \hat{\sigma}_z | -1 -\frac{1}{2} \rangle = \zeta \cdot (-1) \cdot (-\frac{1}{2}) = \frac{1}{2} \zeta \]
\[ H_{23} = \frac{\zeta}{\hbar^2} \langle 1 -\frac{1}{2} | \hat{\sigma}_+ \hat{\sigma}_- | 0 \frac{1}{2} \rangle = \frac{1}{2} \zeta \cdot \sqrt{2} \cdot 1 \langle 1 -\frac{1}{2} | 1 -\frac{1}{2} \rangle = \frac{\sqrt{3}}{2} \zeta = H_{32} \]
\[ H_{45} = \frac{\zeta}{\hbar^2} \langle 0 -\frac{1}{2} | \hat{\sigma}_+ \hat{\sigma}_- | -1 \frac{1}{2} \rangle = \frac{1}{2} \zeta \cdot \sqrt{2} \cdot 1 = \frac{\sqrt{3}}{2} \zeta = H_{54} \]

Diagonalisation of the 2 \times 2 blocks of the \( H \) matrix:

\[
\begin{bmatrix}
-\frac{1}{2} \zeta - E_{(1)} & \sqrt{\frac{1}{2}} \zeta \\
\sqrt{\frac{1}{2}} \zeta & -E_{(1)}
\end{bmatrix}
= (-\frac{1}{2} \zeta - E_{(1)})^{-1}E_{(1)} - \frac{1}{2} \zeta^2 = 0
\]

\[ E_{(1)} = \frac{1}{2} \zeta; \quad E_{(2)} = -\zeta. \]

Evaluation of the zeroth-order functions for \( E_{(1)} = \frac{1}{2} \zeta \):

\[ 0 = (-\frac{1}{2} \zeta - \frac{1}{2} \zeta) u_{2(1)} + \sqrt{\frac{3}{2}} \zeta u_{3(1)} \]
\[ x_{(1)} = \frac{u_{2(1)}}{u_{3(1)}} = \sqrt{\frac{1}{2}}; \quad u_{2(1)} = \sqrt{\frac{1}{3}}; \quad u_{3(1)} = \sqrt{\frac{2}{3}} \]
\[ \psi_2 = \sqrt{\frac{1}{3}} | 1 -\frac{1}{2} \rangle + \sqrt{\frac{2}{3}} | 0 \frac{1}{2} \rangle. \quad (52) \]

For \( E_{(2)} = -\zeta \), the result is:

\[ 0 = (-\frac{1}{2} \zeta + \zeta) u_{2(2)} + \sqrt{\frac{1}{2}} \zeta u_{3(2)} \]
\[ x_{(2)} = \frac{u_{2(2)}}{u_{3(2)}} = -\sqrt{2}; \quad u_{2(2)} = -\sqrt{\frac{2}{3}}; \quad u_{3(2)} = \sqrt{\frac{1}{3}} \]
\[ \psi_3 = -\sqrt{\frac{2}{3}} | 1 -\frac{1}{2} \rangle + \sqrt{\frac{1}{3}} | 0 \frac{1}{2} \rangle. \quad (53) \]

Evaluating the second 2 \times 2 block the resulting states are

\[ E_{(1)} = \frac{1}{2} \zeta : \quad \psi_4 = \sqrt{\frac{1}{3}} | -1 \frac{1}{2} \rangle + \sqrt{\frac{2}{3}} | 0 -\frac{1}{2} \rangle \quad (54) \]
\[ E_{(2)} = -\zeta : \quad \psi_5 = \sqrt{\frac{2}{3}} | -1 \frac{1}{2} \rangle - \sqrt{\frac{1}{3}} | 0 -\frac{1}{2} \rangle. \quad (55) \]

The results are given in Table 6.

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

$$\hat{l}^2 + \hat{l} \cdot \hat{s} + \hat{s} \cdot \hat{l} + \hat{s}^2 = (\hat{l} + \hat{s})^2 = \hat{j}^2.$$  \hfill (56)

If $\hat{j}^2$ acts on a quartet state function $\psi_Q (\psi_1, \psi_2, \psi_4, \psi_6)$ and on a doublet state function $\psi_D (\psi_3, \psi_5)$, respectively, the result is

$$\hat{j}^2 \psi_Q = (\hat{l}^2 + 2 \hat{l} \cdot \hat{s} + \hat{s}^2) \psi_Q = h^2 (2 + 2 \cdot \frac{1}{2} + \frac{3}{2}) \psi_Q = h^2 (\frac{15}{2}) \psi_Q = h^2 (\frac{3}{2}) \psi_Q$$

where $j_2 = \frac{3}{2}$ \hfill (57)

$$\hat{j}^2 \psi_D = (\hat{l}^2 + 2 \hat{l} \cdot \hat{s} + \hat{s}^2) \psi_D = h^2 (2 - 2 \cdot 1 + \frac{3}{2}) \psi_D = h^2 (\frac{3}{2}) \psi_D = h^2 (\frac{1}{2}) \psi_D$$

where $j_1 = \frac{1}{2}$. \hfill (58)

### Table 6: Functions and energies of the spin-orbit coupled p$^1$ system

<table>
<thead>
<tr>
<th>$\psi$</th>
<th>$m_l m_s$</th>
<th>$j m_j$</th>
<th>$m_j = m_l + m_s$</th>
<th>$j$</th>
<th>$E^{(1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$</td>
<td>1 \frac{1}{2} \rangle$</td>
<td>$</td>
<td>\frac{3}{2} \frac{3}{2} \rangle$</td>
<td>$\frac{3}{2}$</td>
</tr>
<tr>
<td>$\psi_2$</td>
<td>$\sqrt{\frac{1}{3}}</td>
<td>1 - \frac{1}{2} \rangle + \sqrt{\frac{2}{3}}</td>
<td>0 \frac{1}{2} \rangle$</td>
<td>$</td>
<td>\frac{3}{2} \frac{1}{2} \rangle$</td>
</tr>
<tr>
<td>$\psi_3$</td>
<td>$\sqrt{\frac{1}{3}}</td>
<td>-1 \frac{1}{2} \rangle + \sqrt{\frac{2}{3}}</td>
<td>0 - \frac{1}{2} \rangle$</td>
<td>$</td>
<td>\frac{3}{2} - \frac{1}{2} \rangle$</td>
</tr>
<tr>
<td>$\psi_4$</td>
<td>$</td>
<td>-1 - \frac{1}{2} \rangle$</td>
<td>$</td>
<td>\frac{3}{2} - \frac{3}{2} \rangle$</td>
<td>$-\frac{3}{2}$</td>
</tr>
<tr>
<td>$\psi_5$</td>
<td>$-\sqrt{\frac{2}{3}}</td>
<td>1 - \frac{1}{2} \rangle + \sqrt{\frac{1}{3}}</td>
<td>0 \frac{1}{2} \rangle$</td>
<td>$</td>
<td>\frac{1}{2} \frac{1}{2} \rangle$</td>
</tr>
<tr>
<td>$\psi_6$</td>
<td>$\sqrt{\frac{2}{3}}</td>
<td>-1 \frac{1}{2} \rangle - \sqrt{\frac{1}{3}}</td>
<td>0 - \frac{1}{2} \rangle$</td>
<td>$</td>
<td>\frac{1}{2} - \frac{1}{2} \rangle$</td>
</tr>
</tbody>
</table>

#### Example 2.3 Spin-orbit coupling of the f$^1$ and the f$^{13}$ system

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

On account of $j = l \pm s = 3 \pm \frac{1}{2}$ (see Example 2.2) for one-electron and one-hole f systems we have

<table>
<thead>
<tr>
<th>$\text{Ln}^{3+}[4f^N]$</th>
<th>ground multiplet</th>
<th>$E$</th>
<th>excited multiplet</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}[4f^1]$</td>
<td>$2F_{5/2}$ ($j = 5/2$)</td>
<td>$-2\zeta_{\text{Ce}}$</td>
<td>$2F_{7/2}$ ($j = 7/2$)</td>
<td>$+\frac{3}{2}\zeta_{\text{Ce}}$</td>
</tr>
<tr>
<td>Yb$^{3+}[4f^{13}]$</td>
<td>$2F_{7/2}$ ($j = 7/2$)</td>
<td>$-\frac{3}{2}\zeta_{\text{Yb}}$</td>
<td>$2F_{5/2}$ ($j = 5/2$)</td>
<td>$+2\zeta_{\text{Yb}}$</td>
</tr>
</tbody>
</table>

Eigenfunctions are obtained with the help of vector coupling coefficients (Clebsch-Gordan coefficients) (see Table 7).
The roots of the lower row of Table 7 become

\[
\begin{array}{ccc}
    j = & m_2 = \frac{1}{2} & m_2 = -\frac{1}{2} \\
    j_1 + \frac{1}{2} & \frac{j_1 + m + \frac{1}{2}}{2j_1 + 1} & \frac{j_1 - m + \frac{1}{2}}{2j_1 + 1} \\
    j_1 - \frac{1}{2} & -\frac{j_1 - m + \frac{1}{2}}{2j_1 + 1} & \frac{j_1 + m + \frac{1}{2}}{2j_1 + 1}
\end{array}
\]

Finally, we obtain

The calculation of the coefficients is demonstrated for \( \left| \frac{5}{2} \frac{5}{2} \right\rangle \) (first line in Table 8).

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 7 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 \( j_1 \rightarrow s \) and \( j_2 \rightarrow l \) the sign of the coefficients has to be changed according to the phase relation \( |j_0 j_0 j_m\rangle = (-1)^{j_0-j_0-j} |j_0 j_0 j_m\rangle \).

Finally, we obtain

\[
\left| \frac{5}{2} \frac{5}{2} \right\rangle = -\sqrt{\frac{6}{7}} \left| 3 - \frac{1}{2} \right\rangle + \sqrt{\frac{1}{7}} \left| 2 + \frac{1}{2} \right\rangle.
\]
Problems

4. 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) $\langle 2, 0 | \hat{l}_+ | 2, 0 \rangle$.

5. The 14 microstates $|m_l m_s\rangle$ of a $f^1$ system ($l = 3$, $s = \frac{1}{2}$) yield under the influence of spin-orbit coupling 14 eigenstates $|j m_j\rangle$ which, apart from the states $|\frac{5}{2} \pm \frac{1}{2}\rangle$, are linear combinations of two microstates each. Use Table 7 to evaluate the vector coupling coefficients for the coupled states $|\frac{5}{2} \frac{1}{2}\rangle$, $|\frac{5}{2} \frac{-1}{2}\rangle$, $|\frac{7}{2} \frac{3}{2}\rangle$, and $|\frac{7}{2} \frac{-3}{2}\rangle$. Control your results with the entries of Table 8.

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?

2.4.2 Magnetic susceptibility, Van Vleck equation

Fundamental magnetisation equation

$$M_m = -N_A \sum_n \left( \frac{\partial E_n}{\partial B} \exp(-E_n/k_B T) \right) \frac{\sum \bar{\mu}_n \exp(-E_n/k_B T)}{\sum \exp(-E_n/k_B T)} = N_A \sum_n \exp(-E_n/k_B T) \sum_n \bar{\mu}_n \exp(-E_n/k_B T)$$

(59)

Van Vleck equation

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

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

$W_n^{(1)}$, $W_n^{(2)}$: First- and second-order Zeeman coefficient

$$\bar{\mu}_n = -\frac{\partial E_n}{\partial B} = -W_n^{(1)} - 2B W_n^{(2)} - \ldots$$

$$\chi_m = \mu_0 N_A \sum_n \left[ \frac{(W_n^{(1)})^2/k_B T - 2W_n^{(2)}}{\sum \exp(-W_n^{(0)}/k_BT)} \right] \exp(-W_n^{(0)}/k_BT)$$

(60)

Eq. (60) is valid for applied magnetic fields $B \to 0$.

Zeeman operator:

one-electron system $\hat{H}_{mag} = -\gamma_e \left( \hat{l} + 2\hat{s} \right) \cdot B$ where $\gamma_e = -e/(2m_e)$

(61)

$$\hat{H}_{mag,z} = -\gamma_e \left( \hat{l}_z + 2\hat{s}_z \right) B_z$$

(62)

single term $\hat{H}_{mag} = -\gamma_e \left( \hat{L} + 2\hat{S} \right) \cdot B$

(63)

$$\hat{H}_{mag,z} = -\gamma_e \left( \hat{L}_z + 2\hat{S}_z \right) B_z$$

(64)

single multiplet $\hat{H}_{mag} = -\gamma_e g_J \hat{J} \cdot B$

(65)

$$\hat{H}_{mag,z} = -\gamma_e g_J \hat{J}_z B_z$$

(66)
Example 2.4 Magnetic susceptibility of the $4f^{1}/4f^{13}$ free ion systems

The 14 spin-coupled eigenfunctions of the $4f^{1}/4f^{13}$ systems are given in Table 8. Applying Zeeman operator (63) the assigned matrix elements in scheme (67) are to be evaluated:

\[
\begin{array}{cccccccc}
\phi_1 & \phi_2 & \phi_3 & \phi_4 & \phi_5 & \phi_6 & \phi_7' & \phi_8' \\
\phi_1' & \phi_2' & \phi_3' & \phi_4' & \phi_5' & \phi_6' & \phi_7 & \phi_8 \\
\phi_1 & \times & \times & \times & \times & \times & \times & \times \\
\phi_2 & \times & \times & \times & \times & \times & \times & \times \\
\phi_3 & \times & \times & \times & \times & \times & \times & \times \\
\phi_4 & \times & \times & \times & \times & \times & \times & \times \\
\phi_5 & \times & \times & \times & \times & \times & \times & \times \\
\phi_6 & \times & \times & \times & \times & \times & \times & \times \\
\phi_7' & \times & \times & \times & \times & \times & \times & \times \\
\phi_8' & \times & \times & \times & \times & \times & \times & \times \\
\end{array}
\]

Calculation of the off-diagonal element \( \langle \phi_2' | \hat{H}_z^{(1)} | \phi_1 \rangle \)

\[
\begin{align*}
\langle \phi_2' | \hat{H}_z^{(1)} | \phi_1 \rangle &= \langle \frac{7}{2}, \frac{5}{2} | - \gamma_e (\hat{l}_z + 2\hat{s}_z) | \frac{5}{2}, \frac{5}{2} \rangle \\
&= -\gamma_e \left[ \frac{\sqrt{6}}{7} \left\langle \frac{3}{2}, -\frac{1}{2} | \hat{l}_z + 2\hat{s}_z | \frac{3}{2}, -\frac{1}{2} \right\rangle + \sqrt{\frac{6}{7}} \left\langle 2 + \frac{1}{2} | \hat{l}_z + 2\hat{s}_z | \frac{3}{2}, -\frac{1}{2} \right\rangle - \frac{\sqrt{6}}{7} \left\langle 2 + \frac{1}{2} | \hat{l}_z + 2\hat{s}_z | 2 + \frac{1}{2} \right\rangle \right] \\
&= -\frac{\gamma_e}{7} \left[ \frac{\sqrt{6}}{7} \left( \frac{3}{2}, -\frac{1}{2} | \hat{l}_z + 2\hat{s}_z | \frac{3}{2}, -\frac{1}{2} \right) - \frac{3}{2} \left| \hat{l}_z + 2\hat{s}_z \right| 2 + \frac{1}{2} \right] \\
&+ 6 \left( \frac{2}{3}, \frac{1}{2} | \hat{l}_z + 2\hat{s}_z | \frac{3}{2}, -\frac{1}{2} \right) + \frac{\sqrt{6}}{7} \left( 2 + \frac{1}{2} | \hat{l}_z + 2\hat{s}_z | 2 + \frac{1}{2} \right) \\
&= -\frac{\sqrt{6}}{7} \mu_B
\end{align*}
\]

We obtain with eq. (32) for \( W_{5/2}^{(2)} \):

\[
W_{5/2}^{(2)} = -\frac{\left| \langle \frac{7}{2}, \frac{5}{2} | - \gamma_e (\hat{l}_z + 2\hat{s}_z) | \frac{5}{2}, \frac{5}{2} \rangle \right|^2}{W_{7/2}^{(0)} - W_{5/2}^{(0)}} = -\frac{(6/49) \mu_B^2}{(7/2) \zeta} = -\frac{12 \mu_B^2}{343 \zeta}.
\]
In this approximation the susceptibility equation reads
\[ \chi_{\text{susceptibility}} = \text{eqn. for the f}^1/\text{f}^{13} \text{ system} \]

In Table 9 the quantities \( W_n^{(0)} \), \( W_n^{(1)} \) and \( W_n^{(2)} \) are collected. The final susceptibility equation for the \( f^1/\text{f}^{13} \) system is obtained by summing up the contributions of the 14 levels:

\[
\chi_m = \mu_0 \frac{N_A \mu_B^2}{3k_B T} \mu_{\text{eff}} \quad \text{where} \quad \mu_{\text{eff}} = \\
\left[ 3 \left( \frac{45}{7} + \frac{16k_B T}{49 \zeta} \right) + 4 \left( \frac{144}{7} - \frac{12k_B T}{49 \zeta} \right) \exp \left( -\frac{7\zeta}{2k_B T} \right) \right]^{-1} \\
3 + 4 \exp \left( -\frac{7\zeta}{2k_B T} \right) \quad (68)
\]

For Ce\(^{3+}\) the parameter \( \zeta \) in eq. (68) refers to the single-electron spin-orbit coupling constant while in the case of Yb\(^{3+}\) the term spin-orbit coupling constant \( \lambda_{LS} = -\zeta \) has to be replaced for \( \zeta \). (Notice that \( \lambda_{LS} = \pm \zeta/(2S) \).)

The absolute energy separation between \( 2F_{5/2} \) and \( 2F_{7/2} \) is \( \frac{7}{2} \times \zeta_{\text{Yb}} = \frac{7}{2} \times 2870 \text{ cm}^{-1} \approx 10\,000 \text{ cm}^{-1} \) for the Yb\(^{3+}\) ion and \( \frac{7}{2} \times \zeta_{\text{Ce}} = \frac{7}{2} \times 625 \text{ cm}^{-1} \approx 2\,200 \text{ cm}^{-1} \) for the Ce\(^{3+}\)-ion. In magnetochemical practice the higher lying multiplet is often ignored in eq. (68). There are two possibilities for simplification:

1.) \( \zeta \rightarrow \infty \) (4f\(^1\)) and \( \lambda_{LS} \rightarrow -\infty \) (4f\(^{13}\)) respectively:

\[
\chi_m(4f^1) = \mu_0 \frac{N_A \mu_B^2}{3k_B T} \left( \frac{45}{7} \right) \quad \text{and} \quad \chi_m(4f^{13}) = \mu_0 \frac{N_A \mu_B^2}{3k_B T} \left( \frac{144}{7} \right) \quad (69)
\]

\[
\mu_{\text{eff}}(4f^1) = \frac{45}{7} = \left( \frac{6}{7} \right)^2 \left( \frac{5}{2} \right) \left( \frac{7}{2} \right) \quad \text{and} \quad \mu_{\text{eff}}(4f^{13}) = \frac{144}{7} = \left( \frac{8}{7} \right)^2 \left( \frac{7}{2} \right) \left( \frac{9}{2} \right) \quad (69)
\]

In this approximation \( \mu_{\text{eff}}^2 \) is temperature independent.

2.) In a less drastic approximation the contribution of the excited multiplet is again neglected, but not \( W^{(2)} \) of the ground multiplet, so that in the case of the 4f\(^1\) system the susceptibility equation reads

\[
\chi_m(4f^1) = \mu_0 \frac{N_A \mu_B^2}{3k_B T} \left\{ \frac{45}{7} + \frac{16k_B T}{49 \zeta} \right\} \quad \text{in general} \quad \chi_m = \mu_0 \frac{N_A g_J^2 (J + 1) \mu_B^2}{3k_B T} + \chi_0 \quad (70)
\]

\( \chi_0 \) is positive, leading to a weak increase of \( \mu_{\text{eff}} \) with increasing temperature.
3 Lanthanide ions in cubic and non-cubic ligand fields

The evaluation of LF effects on f systems requires more effort than on d systems:
- On account of the larger angular momentum quantum number $l$, the number of ligand field parameters is larger, for example two instead of one for cubic symmetry;
- The number of microstates used in complete magnetochemical analyses is larger for f systems (for example 91 microstates for $f^2$ compared to 45 for $d^2$).

Ground multiplets of the $f^1$ to $f^{13}$ ions:

<table>
<thead>
<tr>
<th>$f^N/f^{14-N}$</th>
<th>$f^1/f^{13}$</th>
<th>$f^2/f^{12}$</th>
<th>$f^3/f^{11}$</th>
<th>$f^4/f^{10}$</th>
<th>$f^5/f^9$</th>
<th>$f^6/f^8$</th>
<th>$f^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ground multiplet</td>
<td>$2F_{1/2}/2F_{7/2}$</td>
<td>$3H_{4/2}/3H_6$</td>
<td>$4I_{9/2}/4I_{15/2}$</td>
<td>$5I_{13/2}/5I_{18}$</td>
<td>$6H_{15/2}/6H_{15}$</td>
<td>$7F_0/7F_6$</td>
<td>$8S_{7/2}$</td>
</tr>
</tbody>
</table>

3.1 Ligand-field (LF) operators [7]

General form of the LF operator for one-electron systems:

$$\hat{H}_{\text{LF}} = \sum_{k=0}^{\infty} \sum_{q=-k}^{+k} A^q_k r^k C^k_q(\theta, \phi), \quad \text{where}$$

$$A^q_k = -e(-1)^q \int \frac{\rho(R)}{R^{k+1}} C^k_{-q}(\theta, \phi) d\tau R$$

geometrical coordination factor

and

$$C^k_q = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y^k_q(\theta, \phi)$$

Racah tensor

LF operator for cubic ligand fields:

for $f^1$ system

$$\hat{H}^\text{cub}_{\text{LF}} = A^0_4 r^4 \left[ C^4_0 + \sqrt{5/14} \left( C^4_4 + C^4_{-4} \right) \right] + A^0_6 r^6 \left[ C^6_0 - \sqrt{7/2} \left( C^6_4 + C^6_{-4} \right) \right]$$

for $d^1$ system

$$C^4_0 = \frac{1}{8} \left(35 \cos^4 \theta - 30 \cos^2 \theta + 3\right)$$

$$C^4_{\pm 4} = \frac{1}{16} \sqrt{10} \sin^4 \theta e^{\pm i4\phi}$$

$$C^6_0 = \frac{1}{16} \left(231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5\right)$$

$$C^6_{\pm 4} = \frac{3}{32} \sqrt{14} \sin^4 \theta (11 \cos^2 \theta - 1) e^{\pm i4\phi}$$

General LF matrix element:

$$\int \psi^*_{n,l,m_l}(r, \theta, \phi) \hat{H}_{\text{LF}} \psi_{n,l,m_l'}(r, \theta, \phi) d\tau$$

Specific LF matrix element with $k = 4$ and $q = 0$:

$$\left\{ A^0_4 \int_0^\infty R_{n,l}(r) r^4 R_{n,l}(r) r^2 dR \right\} \int_0^\pi \int_0^{2\pi} Y^4_{m_l}(\theta, \phi) \left[ C^4_0 + \sqrt{5/14} \left( C^4_4 + C^4_{-4} \right) \right] Y^4_{m_l'}(\theta, \phi) \sin \theta d\theta d\phi$$

radial integral $< r^4 >$
\[
\hat{H}_{\text{cub}} = B_0^4 \left[ C_0^4 + \sqrt{5/14} (C_4^4 + C_{-4}^4) \right] + B_0^6 \left[ C_0^6 - \sqrt{7/2} (C_4^6 + C_{-4}^6) \right] \quad (75)
\]

With the help of integrals of the type \(\langle Y_{ml}^{l} | C_k^q | Y_{m'l'}^{l'} \rangle \) [3], listed in Table 10 (p electrons) and Table 13 (f electrons), LF effects can be evaluated. The \(k\) values in eq. (72) comprise terms with \(k \leq 2l\) and \(k\) even. The term with \(k = 0\) has spherical symmetry, produces no splitting and is therefore omitted. The relevant \(k\) values for LF terms are \(k = 2\) (p electrons), \(k = 2, 4\) (d electrons), \(k = 2, 4, 6\) (f electrons). Notice that the operators \(C_k^q\) act only on the orbital part of a wave function.

### 3.2 Introduction: p\(^1\) system

#### 3.2.1 Cylindrical LF: \(\hat{H}_{\text{cyl}}^{\text{LF}} + H_{\text{SO}}\)

**Example 3.1** The \(p^1\) ion in a cylindrical LF

To introduce the use of LF operators and electrostatic matrix elements, the \(p^1\) system in a cylindrical LF (\(D_{\infty h}\)) is discussed\(^4\). The LF operator consists of a single term with \(k = 2\) and \(q = 0\):

\[
\hat{H}_{\text{cyl}}^{\text{LF}} = B_0^2 C_0^2, \quad \text{where} \quad B_0^2 = A_2^0 < r^2 > \quad \text{and} \quad C_0^2 = \frac{1}{2} (3 \cos^2 \theta - 1) \quad (76)
\]

With the help of the matrix components of the electrostatic interactions, shown in Table 10, the \(3 \times 3\) matrix (77) is obtained. Notice that only the red numbers corresponding to \(c^2\) are relevant. Since the operator \(C_0^2\) does not change \(m_l\), matrix elements \(\langle m_l | C_0^2 | m_{l'} \rangle\) with \(m_l \neq m_{l'}\) are automatically zero.

**Table 10:** Matrix components of electrostatic interactions, \(c^k(lm_l, l'm_{l'})\) for \(l = l' = 1; \ c^k(l'm_{l'}, lm_l) = (-1)^{m_l - m_{l'}} c^k(lm_l, l'm_{l'})\). Red numbers are relevant for Examples 3.1 and 3.3, the blue number for Example 3.3 only.

<table>
<thead>
<tr>
<th>(m_l)</th>
<th>(m'_{l'})</th>
<th>(\epsilon^0)</th>
<th>(5 \epsilon^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\pm 1)</td>
<td>(\pm 1)</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(\pm 1)</td>
<td>0</td>
<td>0</td>
<td>(+\sqrt{3})</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>(\pm 1)</td>
<td>(\mp 1)</td>
<td>0</td>
<td>(-\sqrt{6})</td>
</tr>
</tbody>
</table>

*\(^{a)}\) The numerical factor '5' is the denominator for all \(c^k\) values of the column.*

\[
\begin{array}{|c|cc|c|c|}
\hline
m_l & m'_{l'} & |1\rangle & |-1\rangle & |0\rangle \\
\hline
\langle 1 | & -\frac{1}{5} B_0^2 & & \\
\langle -1 | & & -\frac{1}{5} B_0^2 & \\
\langle 0 | & & & \frac{2}{5} B_0^2 \\
\hline
\end{array} \quad (77)
\]

**Results:** (i) All off-diagonal matrix elements are zero; (ii) LF operator eq. (76) splits the threefold degenerate \(p^1\) system (in the absence of spin-orbit coupling) into an orbital doublet \(| \pm 1\rangle\) with energy \(E_{\text{LF}} = -B_0^2/5\) and a singlet \(| 0\rangle\) with energy \(E_{\text{LF}} = 2B_0^2/5\).

\(^4\) Electronic p states are not split by cubic ligand fields.
**Example 3.2** The $p^1$ system under the action of spin-orbit coupling and a cylindrical ligand field (cf. spin-orbit matrix (51))

\[
\hat{H}_{\text{SO}} + \hat{H}_{\text{cyl}} = \xi(r) \mathbf{I} \cdot \mathbf{s} + B_0^2 C_0^2
\]

(78)

| $m_im_s$ | $|1 \frac{1}{2}\rangle$ | $|1 - \frac{1}{2}\rangle$ | $|0 \frac{1}{2}\rangle$ | $|0 - \frac{1}{2}\rangle$ | $|-1 \frac{1}{2}\rangle$ | $|-1 - \frac{1}{2}\rangle$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\langle 1 \frac{1}{2}|$ | $\frac{1}{2} \zeta - B_0^2/5$ |                  |                  |                  |                  |                  |
| $\langle 1 - \frac{1}{2}|$ |                  | $-\frac{1}{2} \zeta - B_0^2/5$ | $\sqrt{\frac{1}{2}} \zeta$ |                  |                  |                  |
| $\langle 0 \frac{1}{2}|$ |                  |                  | $\sqrt{\frac{1}{2}} \zeta$ | $2B_0^2/5$ |                  |                  |
| $\langle 0 - \frac{1}{2}|$ |                  |                  |                  | $2B_0^2/5$ | $\sqrt{\frac{1}{2}} \zeta$ |                  |
| $\langle -1 \frac{1}{2}|$ |                  |                  |                  |                  | $\sqrt{\frac{1}{2}} \zeta$ | $-\frac{1}{2} \zeta - B_0^2/5$ |
| $\langle -1 - \frac{1}{2}|$ |                  |                  |                  |                  |                  | $\frac{1}{2} \zeta - B_0^2/5$ |

\[
H_{11} = \frac{\zeta}{\hbar^2} \langle 1 \frac{1}{2} | \hat{I}_z \hat{s}_z | 1 \frac{1}{2} \rangle + B_0^2 \langle 1 | C_0^2 | 1 \rangle \langle \frac{1}{2} | \frac{1}{2} \rangle = \frac{1}{2} \zeta - B_0^2/5
\]

\[
H_{22} = \frac{\zeta}{\hbar^2} \langle 1 - \frac{1}{2} | \hat{I}_z \hat{s}_z | 1 - \frac{1}{2} \rangle + B_0^2 \langle 1 | C_0^2 | 1 \rangle \langle -\frac{1}{2} | -\frac{1}{2} \rangle = -\frac{1}{2} \zeta - B_0^2/5
\]

\[
H_{33} = \frac{\zeta}{\hbar^2} \langle 0 \frac{1}{2} | \hat{I}_z \hat{s}_z | 0 \frac{1}{2} \rangle + B_0^2 \langle 0 | C_0^2 | 0 \rangle \langle \frac{1}{2} | \frac{1}{2} \rangle = 2B_0^2/5
\]

\[
H_{44} = \frac{\zeta}{\hbar^2} \langle 0 - \frac{1}{2} | \hat{I}_z \hat{s}_z | 0 - \frac{1}{2} \rangle + B_0^2 \langle 0 | C_0^2 | 0 \rangle \langle -\frac{1}{2} | -\frac{1}{2} \rangle = 2B_0^2/5
\]

\[
H_{55} = \frac{\zeta}{\hbar^2} \langle -1 \frac{1}{2} | \hat{I}_z \hat{s}_z | -1 \frac{1}{2} \rangle + B_0^2 \langle -1 | C_0^2 | -1 \rangle \langle \frac{1}{2} | \frac{1}{2} \rangle = -\frac{1}{2} \zeta - B_0^2/5
\]

\[
H_{66} = \frac{\zeta}{\hbar^2} \langle -1 - \frac{1}{2} | \hat{I}_z \hat{s}_z | -1 - \frac{1}{2} \rangle + B_0^2 \langle -1 | C_0^2 | -1 \rangle \langle -\frac{1}{2} | -\frac{1}{2} \rangle = \frac{1}{2} \zeta - B_0^2/5
\]

\[
H_{23} = \frac{\zeta}{\hbar^2} \langle 1 - \frac{1}{2} | \hat{I}_z \hat{s}_z | 0 \frac{1}{2} \rangle = \sqrt{\frac{1}{2}} \zeta = H_{32}
\]

\[
H_{45} = \frac{\zeta}{\hbar^2} \langle 0 - \frac{1}{2} | \hat{I}_z \hat{s}_z | -1 \frac{1}{2} \rangle = \sqrt{\frac{1}{2}} \zeta = H_{54}
\]

Application of scheme eq. (37) on the $2 \times 2$ matrices yields
\[ H_{22} = -\zeta/2 - B_0^2/5, \quad H_{33} = 2B_0^2/5, \quad H_{23} = H_{32} = -\zeta/\sqrt{2} \]

\[ \tan 2\alpha = \frac{2H_{23}}{H_{22} - H_{33}} = \frac{\sqrt{2}\zeta}{\zeta/2 + 3B_0^2/5} = \frac{\sqrt{2}}{\frac{1}{2} + \frac{3}{5}B_0^2/\zeta} \]  

(79)

**Result:** The combined effect of \( H_{\text{SO}} + H_{\text{LF}}^{\text{vl}} \) splits the sixfold degenerate spin orbital states into three doublets. The composition of the wave functions depends on the ratio \( B_0^2/\zeta \). No simple closed expressions can be given for the functions.

### 3.2.2 Orthorhombic LF: \( H_{\text{LF}}^{\text{or}} + H_{\text{SO}} \)

**Example 3.3** The \( p^1 \) system in orthorhombic ligand fields

\[ \hat{H}_{\text{LF}}^{\text{or}} = B_0^2 C_0^2 + B_2^2 (C_2^2 + C_{-2}^2) \quad \text{where} \quad C_{\pm 2}^2 = \sqrt{\frac{3}{8}} \sin^2 \theta \exp(\pm 2i\phi) \]  

(80)

| \( m_l \) | \( |1\rangle \) | \( |-1\rangle \) | \( |0\rangle \) |
|---|---|---|---|
| \( \langle 1 | \) | \(-\frac{1}{5}B_0^2 \) | \(-\frac{\sqrt{6}}{5}B_2^2 \) |
| \( \langle -1 | \) | \(-\frac{\sqrt{6}}{5}B_2^2 \) | \(-\frac{1}{5}B_0^2 \) |
| \( \langle 0 | \) | \( \frac{2}{5}B_0^2 \) |

Matrix elements of operator eq. (80):

Determination of the correct zeroth order functions by application of scheme eq. (37):

\[ H_{11} = H_{22} = -B_0^2/5, \quad H_{12} = H_{21} = -\sqrt{6}B_2^2/5 \]

\[ \tan 2\alpha = \frac{2H_{12}}{H_{11} - H_{22}} = \frac{-2\sqrt{6}B_2^2/5}{-B_0^2/5 + B_0^2/5} = \frac{-2\sqrt{6}B_2^2/5}{0} = \begin{cases} +\infty & \text{for } B_2^2 < 0 \\ -\infty & \text{for } B_2^2 > 0 \end{cases} \]

\[ 2\alpha = \pm 90^\circ \rightarrow \alpha = \pm 45^\circ; \quad \cot 45^\circ = \pm 1 \]

\[ E_{1,2} = -B_0^2/5 \pm \sqrt{6}B_2^2/5, \quad \Psi_{1,2} = (\sqrt{2})^{-1}(|1\rangle \mp |-1\rangle) \]

\[ E_3 = 2B_0^2/5, \quad \Psi_3 = |0\rangle \]

**Result:** Neglecting spin, the orthorhombic ligand field splits the threefold degenerate orbital states into three singlets.

**Example 3.4** The \( p^1 \) system under the action of spin-orbit coupling and an orthorhombic ligand field

\[ \hat{H}_{\text{SO}} + \hat{H}_{\text{LF}}^{\text{or}} = \xi(r) \hat{\mathbf{I}} \cdot \hat{\mathbf{s}} + B_0^2 C_0^2 + B_2^2 (C_2^2 + C_{-2}^2) \]  

(81)

The matrix elements of this operator are stated in scheme (82). The \(-E^{(1)}\)'s in the diagonal elements are omitted and also the multiplicative factor \( hc \) for the spin-orbit coupling matrix elements which are usually given in the energy equivalent cm\(^{-1}\). The empty off-diagonal elements are automatically zero. The diagonalisation of the 3 × 3
blocks, the energies and the composition of the wave functions must be calculated with the aid of a computer.

<table>
<thead>
<tr>
<th>(m_l m_s)</th>
<th>(1 \frac{1}{2})</th>
<th>(0 - \frac{1}{2})</th>
<th>(-1 \frac{1}{2})</th>
<th>(1 - \frac{1}{2})</th>
<th>(0 \frac{1}{2})</th>
<th>(-1 \frac{1}{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle 1 \frac{1}{2}\rangle)</td>
<td>(\frac{1}{2} \zeta - B_0^2/5)</td>
<td>0</td>
<td>(-\sqrt{6}B_2^2/5)</td>
<td>0</td>
<td>(-\sqrt{6}B_2^2/5)</td>
<td>0</td>
</tr>
<tr>
<td>(\langle 0 - \frac{1}{2}\rangle)</td>
<td>0</td>
<td>(2B_0^2/5)</td>
<td>(\sqrt{\frac{1}{2}} \zeta)</td>
<td>(\sqrt{\frac{1}{2}} \zeta)</td>
<td>(2B_0^2/5)</td>
<td>0</td>
</tr>
<tr>
<td>(\langle -1 \frac{1}{2}\rangle)</td>
<td>(-\sqrt{6}B_2^2/5)</td>
<td>(\sqrt{\frac{1}{2}} \zeta)</td>
<td>(-\frac{1}{2} \zeta - B_0^2/5)</td>
<td>0</td>
<td>(-\sqrt{6}B_2^2/5)</td>
<td>(\frac{1}{2} \zeta - B_0^2/5)</td>
</tr>
</tbody>
</table>

3.3 Cubic LF

3.3.1 Group theoretical tools I [9, 8]

Character tables of the point groups serve to assign the LF states with respect to symmetry and degeneration. For the cubic systems O and T\(_d\) Table 11 is relevant. It is applicable to Ln ions with integer \(J\). The degree of degeneration of the LF states is responsible for the orbital contribution of the lanthanides' magnetic moment: The singlet states \(A_1(\Gamma_1)\) and \(A_2(\Gamma_2)\) as well as the doublet state \(E(\Gamma_3)\) are non-magnetic, while the triplet states \(T_1(\Gamma_4)\) and \(T_2(\Gamma_5)\) are magnetic. For half-integer \(J\) all states are on principle magnetic; for cubic LF character tables of the respective double groups O' and T\(_d\) are relevant [8, 10] (cf. Table 12). Usually Bethe's nomenclature is used for f systems, see, e.g., the article of Lea, Leask, Wolf (LLW[16]).

### Tab. 11: Character table of the symmetry groups O and T\(_d\)

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>E</th>
<th>8 C(_3)</th>
<th>3 C(_2)</th>
<th>6 C(_4)</th>
<th>6 C(_2)'</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(_d)</td>
<td>E</td>
<td>8 C(_3)</td>
<td>3 C(_2)</td>
<td>6 S(_4)</td>
<td>6 (\sigma_d)</td>
<td></td>
</tr>
<tr>
<td>(A_1) (^a))</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(\Gamma_1) (^b))</td>
</tr>
<tr>
<td>(A_2)</td>
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<td>1</td>
<td>(-1)</td>
<td>(-1)</td>
<td>(\Gamma_2)</td>
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<td>2</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
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<td>(-1)</td>
<td>1</td>
<td>(-1)</td>
<td>(\Gamma_4)</td>
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<tr>
<td>(T_2)</td>
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<td>(-1)</td>
<td>(-1)</td>
<td>1</td>
<td>(\Gamma_5)</td>
</tr>
</tbody>
</table>

\(^a\)) Mulliken nomenclature.

\(^b\)) Bethe nomenclature.

3.3.2 4f\(^1\) system (Ce\(^{3+}\), \(2F\): \(H_{SO} + H_{LF}^{cub}\))

Ce\(^{3+}\) is a half-integer system. So, O', T\(_d\)' are relevant. Under the action of the LF operator

\[
\hat{H}_{LF}^{cub}(4f^1) = B_0^6 \left\{ C_0^4 + \frac{5}{11} [C_4^4 + C_{-4}^4] \right\} + \left( \frac{B_0^6}{2} \right) \left\{ C_0^6 - \sqrt{\frac{5}{11}} [C_4^6 + C_{-4}^6] \right\},
\]

irrelevant for restricted basis \(2F_{5/2}\)

the free ion multiplets split according to \(2F_{5/2} \rightarrow G' (\Gamma_8) + E'' (\Gamma_7)\) and \(2F_{7/2} \rightarrow G' (\Gamma_8) + E'' (\Gamma_7) + E' (\Gamma_6)\). If \(H_{SO}\) is distinctly stronger than \(H_{LF}\) it is convenient to consider
Table 12: Character table of the double groups O' and T_d

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>R</th>
<th>4C_3</th>
<th>4C_3^2</th>
<th>3C_2</th>
<th>3C_4</th>
<th>3C_4^3</th>
<th>6C_2'</th>
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</thead>
<tbody>
<tr>
<td>O'</td>
<td></td>
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<td></td>
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</tr>
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<td></td>
</tr>
<tr>
<td>T_d</td>
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</tr>
<tr>
<td>A_1(Γ_1)^a)</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>-1</td>
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<td>0</td>
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<td>-1</td>
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<td>T_2(Γ_5)</td>
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<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

^a) Γ_1 − Γ_5: integer J; Γ_1 − Γ_3: non-magnetic.
^b) Γ_6 − Γ_8: half-integer J; magnetic.

$H_{LF}$ acting only on the ground multiplet $^2F_{5/2} → G'(Γ_8) + E''(Γ_7)$. This approximation has the advantage that $H_{LF}^{cub}$ can be restricted to the fourth degree term ($k = 4$), since the corresponding LF matrix elements of the sixth degree term are zero. Using Table 8 and Table 13 the matrix elements of $H_{LF}^{cub}$ in scheme (83) are obtained.

Normally, the spin-orbit coupled states $|J M_J⟩$ are used as a basis for the multiplet. In the following examples, however, we write them as $|M_L M_S⟩$ basis with the advantage that the action of $H_{LF}^{cub}$ on the orbital function $|M_L⟩$ becomes obvious.

Table 13: Matrix components of electrostatic interactions, $c^k(l m_l, l'm_{l'})$ for $l = l' = 3$; $c^k(l m'_l, l m_l) = (−1)^{m_l − m_l'}c^k(l m_l, l'm_{l'})$ [3]

<table>
<thead>
<tr>
<th>m_l</th>
<th>m_l'</th>
<th>c^0</th>
<th>15 c^2</th>
<th>33 c^4</th>
<th>429/5 c^6</th>
<th>m_l</th>
<th>m_l'</th>
<th>c^0</th>
<th>15 c^2</th>
<th>33 c^4</th>
<th>429/5 c^6</th>
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<td>-5</td>
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<td>+5</td>
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<td>0</td>
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<td>0</td>
<td>-√24</td>
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</tr>
</tbody>
</table>

^a) The numerical factor is the denominator for all $c^k$ values of a column. (Notice that only the red terms are relevant in Example 3.5.)
Example 3.5 Evaluation of the diagonal element $H_{11} = \langle \frac{5}{2} | \hat{H}_{\text{LF}}^{\text{cub}} | \frac{5}{2} \rangle$ of matrix (83)

$$H_{11} = \frac{1}{7} \langle -\sqrt{6} \langle 3, -\frac{1}{2} \rangle + \langle 2, \frac{1}{2} | \hat{H}_{\text{LF}}^{\text{cub}} | -\sqrt{6} | 3, -\frac{1}{2} \rangle + | 2, \frac{1}{2} \rangle \rangle$$

(i) 'Integration' with respect to the spin, (ii) insert of $c^k(lm_l, l'm'_l)$ values$^{5}$:

$$H_{11} = \frac{1}{7} \left( 6 \langle 3 | \hat{H}_{\text{LF}}^{\text{cub}} | 3 \rangle + \langle 2 | \hat{H}_{\text{LF}}^{\text{cub}} | 2 \rangle \right) = \frac{1}{7} \left[ B_0^4 \left( 6 \langle 3 | C_0^4 | 3 \rangle + \langle 2 | C_0^4 | 2 \rangle \right) + B_0^6 \left( 6 \langle 3 | C_6^4 | 3 \rangle + \langle 2 | C_6^4 | 2 \rangle \right) \right] = \frac{1}{21} B_0^4.$$

<table>
<thead>
<tr>
<th>$4f^1(\text{cub})$</th>
<th>$\langle \frac{5}{2} \rangle$</th>
<th>$-\frac{3}{2}$</th>
<th>$\langle -\frac{3}{2} \rangle$</th>
<th>$\langle \frac{3}{2} \rangle$</th>
<th>$\langle -\frac{3}{2} \rangle$</th>
<th>$\langle \frac{1}{2} \rangle$</th>
<th>$\langle -\frac{1}{2} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \frac{5}{2} \rangle$</td>
<td>$\frac{1}{21}$</td>
<td>$\frac{\sqrt{6}}{21}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\langle -\frac{3}{2} \rangle$</td>
<td></td>
<td>$\frac{\sqrt{5}}{21}$</td>
<td>$\frac{5}{21}$</td>
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<tr>
<td>$\langle -\frac{5}{2} \rangle$</td>
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<td>$\frac{1}{21}$</td>
<td>$\frac{\sqrt{5}}{21}$</td>
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</tr>
<tr>
<td>$\langle -\frac{3}{2} \rangle$</td>
<td></td>
<td></td>
<td></td>
<td>$\frac{\sqrt{5}}{21}$</td>
<td>$\frac{5}{21}$</td>
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<tr>
<td>$\langle \frac{1}{2} \rangle$</td>
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<td></td>
<td></td>
<td>$\frac{\sqrt{5}}{21}$</td>
<td>$\frac{5}{21}$</td>
<td></td>
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<tr>
<td>$\langle -\frac{1}{2} \rangle$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\frac{2}{21}$</td>
</tr>
</tbody>
</table>

$H_{\text{LF}}$ matrix of $^2F_{5/2}$

(83)

Example 3.6 Evaluation of the off-diagonal element $\langle \frac{5}{2} | \hat{H}_{\text{LF}}^{\text{cub}} | -\frac{3}{2} \rangle$

$$H_{12} = \frac{1}{7} \langle -\sqrt{6} \langle 3, -\frac{1}{2} \rangle + \langle 2, \frac{1}{2} | \hat{H}_{\text{LF}}^{\text{cub}} | -\sqrt{2} | -1, -\frac{1}{2} \rangle + \sqrt{5} | -2, \frac{1}{2} \rangle \rangle$$

$$H_{12} = \frac{1}{7} \left( \sqrt{12} \langle 3 | \hat{H}_{\text{LF}}^{\text{cub}} | -1 \rangle + \sqrt{5} \langle 2 | \hat{H}_{\text{LF}}^{\text{cub}} | -2 \rangle \right) = \frac{1}{7} \left[ B_0^4 \sqrt{\frac{5}{14}} \left( \sqrt{12} \langle 3 | C_0^4 | -1 \rangle + \sqrt{5} \langle 2 | C_0^4 | -2 \rangle \right) \right] = \frac{\sqrt{5}}{21} B_0^4$$

The $H_{\text{LF}}$ matrix (83) has two identical $1 \times 1$ and two identical $2 \times 2$ blocks. The former two correspond to the $|M_J\rangle$ states $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ yielding the first-order correction to the energy $E^{(1)} = E_{\text{LF}} = (2/21) B_0^4$. The energy of the other states is obtained by applying eqn. (36):

$$\begin{bmatrix}
\frac{1}{21} B_0^4 - E & \frac{\sqrt{5}}{21} B_0^4 \\
\frac{\sqrt{5}}{21} B_0^4 & -\frac{3}{21} B_0^4 - E
\end{bmatrix} = 0 \quad \Rightarrow \quad \begin{cases}
E_1 = \frac{2}{21} B_0^4 \\
E_2 = -\frac{4}{21} B_0^4.
\end{cases}$$

$^5$) Note that the sixth degree term ($k = 6$) of $\hat{H}_{\text{LF}}^{\text{cub}}$, applied to $^2F_{5/2}[nf^1]$, has no influence, that is, the corresponding matrix elements vanish.
The sixfold degenerate multiplet $^{2}F_{5/2}$ is split by a cubic LF in a doublet $(E''; \Gamma_{7})$ and a quartet $(G''; \Gamma_{8})$ (see Table 14). In octahedral surrounding with negatively charged ligands $E''$ is the ground state ($A_{4}^{0}, B_{4}^{0} > 0$), whereas in tetrahedral symmetry the splitting pattern is reversed. The splitting $\Delta E(G', E'') = (6/21) B_{0}^{4}$ is in the range of a few 100 cm$^{-1}$, that is, several orders of magnitude smaller than for d ions, caused by smaller radial integrals and larger metal–ligand distances for the 4f ions.

Table 14: Wavefunctions and energies of the $^{2}F_{5/2}$ multiplet perturbed by a cubic LF

| $\Gamma M$ $^{a,b)}$ | $|M_{J}\rangle$ | $E_{LF}$ |
|------------------|-----------------|--------|
| $|G'\kappa, \mu\rangle$ | $\pm \sqrt{\frac{\sqrt{5}}{2}} \pm \frac{\sqrt{5}}{2}$ $\pm \sqrt{\frac{1}{6}} \pm \frac{3}{2}$ | $\frac{2}{21} B_{0}^{4}$ |
| $|G'\lambda, \nu\rangle$ | $\pm \sqrt{\frac{1}{2}}$ | |
| $|E''\alpha''\beta''\rangle$ | $\sqrt{\frac{1}{6}} \pm \frac{5}{2}$ $\pm \sqrt{\frac{3}{2}}$ | | $-\frac{4}{21} B_{0}^{4}$ |

$a)$ $G' \equiv \Gamma_{8}; \quad E'' \equiv \Gamma_{7}.$  
$b)$ For the states in short cf. ref. [6].  
$c)$ Phase for Kramers doublets:  

$$|\xi\rangle = \sum_{J,M} C_{J,M} |JM\rangle |\xi\rangle = \sum_{J,M} C_{J,M}^{*} (-1)^{J-M} |J-M\rangle.$$  

Magnetic susceptibility

Zeeman operator (eq. (66)):  

$$\hat{H}_{mag,z} = -\gamma_{e} g_{J} \hat{J}_{z} B_{z} \quad \text{where} \quad \gamma_{e} = -e/(2m_{e}), \quad g_{J} = 6/7$$

Application of the $z$ component of the Zeeman operator onto the six symmetry-adapted linear combinations of the ground multiplet $^{2}F_{5/2}$ (Table 14) yields the matrix elements in Table 15 (in units of $g_{J} \mu_{B} B_{z}$ and $\Delta = E_{LF}(G') - E_{LF}(E'') = (6/21) B_{0}^{4}$).

Table 15: $W_{n}^{(0)}$, $W_{n}^{(1)}$ and $W_{n}^{(2)}$ of the 4f$^{1}$ system perturbed by $H_{LF}^{cub}$ ($\Delta \equiv (6/21) B_{0}^{4}$)

<table>
<thead>
<tr>
<th>$\equiv G'\kappa, \nu$</th>
<th>$W_{n}^{(0)}$</th>
<th>$W_{n}^{(1)}$</th>
<th>$W_{n}^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\equiv G'\lambda, \mu$</td>
<td>$\pm \frac{11}{6}$</td>
<td>$\pm \frac{20}{9 \Delta}$</td>
<td>$\pm \frac{1}{2}$</td>
</tr>
<tr>
<td>$\equiv E''\bar{M}''$</td>
<td>$0 \pm \frac{5}{6}$</td>
<td>$\frac{20}{9 \Delta}$</td>
<td></td>
</tr>
</tbody>
</table>

Diagonal element:

$$H_{11} = \langle G'\kappa | \hat{H}_{mag,z} | G'\kappa \rangle$$

$$= \left[ (\frac{5}{6}) (\frac{5}{2}) + (\frac{1}{6}) (-\frac{3}{2}) \right] g_{J} \mu_{B} B_{z} = (\frac{11}{6}) g_{J} \mu_{B} B_{z}$$

Off-diagonal element:

$$H_{15} = \langle G'\kappa | \hat{H}_{mag,z} | E''\alpha'' \rangle$$

$$= \left[ \sqrt{\frac{1}{6}} \sqrt{\frac{5}{6}} (\frac{5}{2}) - \sqrt{\frac{1}{6}} \sqrt{\frac{5}{6}} (-\frac{3}{2}) \right] g_{J} \mu_{B} B_{z} = (\frac{2\sqrt{5}}{3}) g_{J} \mu_{B} B_{z}.$$
Substitution of $W_n^{(0)}$, $W_n^{(1)}$, and $W_n^{(2)}$ into the VanVleck eq. (60) yields the magnetic susceptibility of the 4f system in cubic ligand fields:

$$\chi_m = \mu_0 N_A \mu_B^2 \frac{\mu_{\text{eff}}}{3k_B T}$$

where

$$\mu_{\text{eff}}^2 = \frac{g^2}{12} \left[ 25 + \frac{40}{3\Delta} k_B T + \left( \frac{130}{12} - \frac{40}{3\Delta} k_B T \right) \exp \left( \frac{-\Delta}{k_B T} \right) \right] \left[ 1 + 2 \exp \left( \frac{-\Delta}{k_B T} \right) \right].$$

Fig. 8 shows the $\mu_{\text{eff}} - T$ and the $\chi_m^{-1} - T$ behaviour for $\Delta = +605 \text{ cm}^{-1}$ (LF ground state $E''(\Gamma_7)$, $B_0^4 = 2119 \text{ cm}^{-1}$, oct.) and $\Delta = -605 \text{ cm}^{-1}$ ($G'(\Gamma_8)$, $B_0^4 = -2119 \text{ cm}^{-1}$, tetrah., cube).

Fig. 8: Ce$^{3+}$ in cubic LF; $\mu_{\text{eff}} - T$ (a,c,e) and $\chi_m^{-1} - T$ diagrams (b,d,f); $\Delta = 605 \text{ cm}^{-1}$ oct., (e,f), $\Delta = -605 \text{ cm}^{-1}$ tetrah., cube, (c,d); straight lines (a,b) correspond to the free ion.

**Discussion**

1. The ligand field effect produces a distinct deviation from free ion magnetic behaviour, except Ln ions with 4f$^7$ configuration (Eu$^{2+}$, Gd$^{3+}$).

2. At very low temperature the $\chi_m^{-1}$ vs. $T$ curves for systems with an odd number of 4f electrons (half-integral $J$) become nearly straight lines running into the origin (Curie-like behaviour, explicable with eq. (84)), provided that cooperative magnetic effects are absent.

3. In the case of integral $J$ the low-temperature magnetic behaviour is more complicated (see Section 3.3.4).

4. **Warning**: The upper region of the $\chi_m^{-1}$ versus $T$ curves does not follow the Curie or Curie-Weiss law (except 4f$^7$ ions). To compare the magnetic behaviour of Ln ions in a crystal with that of free ions, the $\mu_{\text{eff}}$ versus $T$ plot is suited.
5. Cooperative effects between magnetically active ions can be described by a so-called molecular-field parameter $\lambda_{MF}$:

$$\chi_m^{-1} = \chi_m^{-1}(LF) - \lambda_{MF}. \quad (85)$$

6. Susceptibility equations of the type (84) are not only suited for molecular and ionic systems, but also for intermetallics with stable Ln valence. The 6s and 5d valence electrons are delocalized to a high degree and yield normally only a small TIP.

7. Ce, Yb, Eu are candidates for mixed-valence behaviour ($\text{Ce}^{3+/4+}$, $\text{Yb}^{2+/3+}$, $\text{Eu}^{2+/3+}$).

**Paramagnetism of $\text{Ce}^{3+}$, $\text{Yb}^{3+}$, $\text{U}^{5+}$ ions in an octahedral LF**

Figs. 9 and 10 exhibit the typical paramagnetic behaviour of octahedrally coordinated Ce(III), Yb(III) and U(V) compounds as $\chi_m^{-1}-T$ and $\mu_{\text{eff}}-T$ plots calculated with program CONDON [12], using the parameter values (in cm$^{-1}$):

- Ce(III): $B_4^0 = 2119$, $B_6^0 = 261$, $\zeta = 623$, see Tab. 16 [13];
- Yb(III): $B_4^0 = 1471$, $B_6^0 = 0$, $\zeta = 2903$ [13];
- U(V): $B_4^0 = 23100$, $B_6^0 = 3750$, $\zeta = 2200$ [14].

The 4f$^{13}$ ion with ground multiplet $^2F_{7/2}$ is the strongest paramagnet, the 5f$^1$ ion ($^2F_{5/2}$) the weakest one. The lower $\mu_{\text{eff}}$ value of the latter compared to $\mu_{\text{eff}}$ of Ce(III) is the consequence of the much stronger LF effect.

**Fig. 9:** Typical $\chi_m^{-1}-T$ diagrams of compounds with Ce(III), Yb(III) and U(V) in an octahedral ligand field.

**Fig. 10:** Typical $\mu_{\text{eff}}-T$ diagrams of compounds with Ce(III), Yb(III) and U(V) in an octahedral ligand field.

### 3.3.3 4f$^N$ systems

For many-electron lanthanide systems $\hat{H}_{\text{LF}}^{\text{cub}}$ reads

$$\hat{H}_{\text{LF}}^{\text{cub}}(4f^N) = B_4^0 \sum_{i=1}^{N} \left\{ C_0^4(i) + \sqrt{\frac{5}{14}} [C_4^4(i) + C_{-4}^4(i)] \right\} + B_6^0 \sum_{i=1}^{N} \left\{ C_0^6(i) - \frac{\sqrt{7}}{2} [C_4^6(i) + C_{-4}^6(i)] \right\} \quad (86)$$
Coupling schemes: The 4f states are controlled by $H_{ee}$, $H_{SO}$ (see Fig. 11) and the ligand field $H_{LF}$, where the order of energetic effects is $H_{ee} > H_{SO} > H_{LF}$ (except for the 4f$^4$, 4f$^5$, 4f$^6$ systems where $H_{SO} \approx H_{LF}$). To describe the electronic situation, three coupling schemes are distinguished, depending on the relative strength of $H_{LF}$ and on the desired accuracy in LF parameter determination [15].

![Energy levels of selected Ln$^{3+}$ ions](image)

Fig. 11: Energies of ground state multiplets of selected Ln$^{3+}$ ions ($k_B T = 208.6 \text{ cm}^{-1}$ at 300 K)

- **Russell-Saunders coupling scheme (LS coupling scheme)**
  Including spin-orbit coupling in 1st order, S, L, and J are good quantum numbers in this coupling scheme, i.e., this model requires multiplets $2S+1L_J$ that are (i) well separated in energy and (ii) only slightly influenced by $H_{LF}$. To estimate LF parameters it is sufficient to study the action of $H_{LF}$ solely on the ground multiplet $2S+1L_J$ [16] (except the 4f$^4$, 4f$^5$, 4f$^6$ systems).

- **Intermediate coupling scheme**
  The intermediate coupling scheme is applicable, if S and L are no longer good quantum numbers on account of the competing perturbations by $H_{ee}$ and $H_{SO}$ while J remains a good quantum number. This model is adequate, if the ligand field splitting is not too strong, i.e., in the case of the weak-field lanthanide system [8]. Examples: lanthanide chlorides and bromides (Cl$^-$, Br$^-$).

- **J-mixing scheme**
  The J-mixing coupling scheme is favourable for strong-field lanthanide systems. If J-mixing, caused by $H_{LF}$, is considered, a $2S+1L_J$ multiplet may have contributions from terms with other J values, that is, J is no longer a good quantum number. Examples: lanthanide oxides and fluorides (O$^{2-}$, F$^-$).

---

6) For lanthanides the term crystal field is often used instead of ligand field.
7) For actinides in high oxidation states there is no energetic order, that is, $H_{ee} \approx H_{SO} \approx H_{LF}$.
8) The terms 'weak field' and 'strong field' here have another meaning than for transition metal compounds. For a strong-field transition metal system, $H_{LF}$ is a stronger interaction than $H_{ee}$ whereas for lanthanides $H_{LF}$ is always weaker than $H_{ee}$.
3.3.4 Magnetic behaviour of the series Cs$_2$NaLnCl$_6$ (overview)

On the basis of spectroscopic data of the series Cs$_2$NaLnCl$_6$\textsuperscript{9)}\textsuperscript{[13]} (see Tab. 16) the magnetic behaviour is calculated with program CONDON\textsuperscript{10)}, developed by Schilder and Lueken [12]. The $\mu_{\text{eff}}$–$T$ data for the representative metal ions Pr$^{3+}$[4f$^2$], Nd$^{3+}$[4f$^3$], Sm$^{3+}$[4f$^5$] and Eu$^{3+}$[4f$^6$] are compared with those of the free ions.

![Fig. 12: Cs$_2$NaLnCl$_6$: unit cell of the elpasolite type](image)

**Table 16:** LF parameters $B_0^4$ and $B_0^6$ of octahedrally coordinated Ln$^{3+}$ ions in Cs$_2$NaLnCl$_6$

<table>
<thead>
<tr>
<th>Ln$^{3+}$</th>
<th>$B_0^4$</th>
<th>$B_0^6$</th>
<th>Ln$^{3+}$</th>
<th>$B_0^4$</th>
<th>$B_0^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}$</td>
<td>2119</td>
<td>261</td>
<td>Tb$^{3+}$</td>
<td>1624</td>
<td>150</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>1938</td>
<td>290</td>
<td>Dy$^{3+}$</td>
<td>1614</td>
<td>148</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>1966</td>
<td>258</td>
<td>Ho$^{3+}$</td>
<td>1593</td>
<td>171</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>(1671)$^b$</td>
<td>(228)$^b$</td>
<td>Er$^{3+}$</td>
<td>1492</td>
<td>163</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>2055</td>
<td>308</td>
<td>Tm$^{3+}$</td>
<td>1498</td>
<td>159</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>1776</td>
<td>136</td>
<td>Yb$^{3+}$</td>
<td>1471</td>
<td>[0]</td>
</tr>
</tbody>
</table>

$^a)$ Values in cm$^{-1}$.

$^b)$ Values for Cs$_2$NaYCl$_6$ : Sm$^{3+}$.

The chemical environment of the Ln ions, compared to the one of d ions, has only a minor effect on the 4f electrons. The LF effect produces splittings of $H_{\text{LF}} \approx 10^2$ cm$^{-1}$

\textsuperscript{9)} Elpasolite type structure, Ln$^{3+}$ point symmetry O$_h$.

\textsuperscript{10)} CONDON considers ligand field effects on the $J$-mixing level and, beyond this model, the applied field dependence of the magnetic susceptibility as well as intermolecular spin-spin exchange couplings.
leading generally to paramagnetism, described by the temperature dependence of the effective Bohr magneton number $\mu_{\text{eff}}$:

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

As a rule, $\mu_{\text{eff}}$ approaches the free Ln ion value for $T > 200$ K (see Table 2, Figs. 8, 10, 13, 14).

Pr$^{3+}$: Applying $B_0^4 = 1938 \text{ cm}^{-1}$ and $B_0^6 = 290 \text{ cm}^{-1}$ the $\chi_m^{-1} - T$ plot in Fig. 13 (left) is obtained. The octahedral LF effect produces temperature independent paramagnetism below 100 K in agreement with the predicted non-magnetic ground state A$_1$ (see Table 17).

Nd$^{3+}$: The magnetic behaviour of Cs$_2$NaNdCl$_6$ exhibits Curie paramagnetism in the temperature range under investigation (see Fig. 13, right). This behaviour is expected for Ln ions with an odd number of 4f electrons in magnetically diluted systems without cooperative interactions.

Sm$^{3+}$: On account of low lying multiplets, $\mu_{\text{eff}}$ of the free Sm$^{3+}$ ion is already temperature dependent (see Fig. 14 (left), curve b, and Fig. 11). After switching on the cubic ligand field (curve a), a drastic modification is observed at $T < 200$ K.

Eu$^{3+}$: In the complete temperature range the magnetic properties of Eu$^{3+}$ compounds are determined by the TIP on account of the non-magnetic ground multiplet with $J = 0$ (see Fig. 14, right). The effect of a cubic ligand field is negligible.

**Fig. 13:** $\chi_m^{-1} - T$ and $\mu_{\text{eff}} - T$ diagrams for Pr$^{3+}$ (left) and Nd$^{3+}$ (right), calculated with the spectroscopically determined data of Cs$_2$NaPrCl$_6$ and Cs$_2$NaNdCl$_6$, respectively (solid lines: full basis; dottet lines: ground multiplet only; dashed lines: free ions)
Fig. 14: $\mu_{\text{eff}}$-$T$ (left) and $\chi^{-1}_m$-$T$ diagrams (right) for Sm$^{3+}$ and Eu$^{3+}$, calculated with the spectroscopically determined data of Cs$_2$NaYCl$_6$:Sm$^{3+}$ (a) and Cs$_2$NaEuCl$_6$ (d), respectively; free Sm$^{3+}$ ion (b), free Eu$^{3+}$ ion (c).

### 3.3.5 4f$^2$ system (Pr$^{3+}$, $^3H_4$: $H_{\text{LF}}^{\text{cub}}$)

For a 4f$^2$ system $H_{\text{LF}}^{\text{cub}}$ reads:

$$
H_{\text{LF}}^{\text{cub}}(4f^2) = B_0^4 \sum_{i=1}^{2} \left\{ C_0^4(i) + \sqrt{\frac{5}{14}} [C_4^4(i) + C_{-4}^4(i)] \right\} + B_0^6 \sum_{i=1}^{2} \left\{ C_6^6(i) - \sqrt{\frac{7}{2}} [C_4^6(i) + C_{-4}^6(i)] \right\}
$$

Compared to the two multiplets of the 4f$^1$ (Ce$^{3+}$) free ion, the 4f$^2$ (Pr$^{3+}$) free ion has 13 multiplets and, in consequence, exhibits a more complicated LF splitting pattern (see Table 17 and ref. [13]).

#### Table 17: Spectroscopically determined levels of the Pr$^{3+}$ ion (O$_h$, octahedron) in Cs$_2$NaPrCl$_6$. The energy increases from top to bottom and from left to right.

<table>
<thead>
<tr>
<th>$^3H_4$</th>
<th>$^3H_5$</th>
<th>$^3H_6$</th>
<th>$^3F_2$</th>
<th>$^3F_3$</th>
<th>$^3F_4$</th>
<th>$^1G_4$</th>
<th>$^1D_2$</th>
<th>$^3P_0$</th>
<th>$^3P_1$</th>
<th>$^1I_6$</th>
<th>$^3P_2$</th>
<th>$^1S_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1<a href="0%5Ea">\Gamma_1</a>$</td>
<td>$T_1^{(1)}$</td>
<td>E $^c$</td>
<td>E $^c$</td>
<td>T$^c$</td>
<td>E $^c$</td>
<td>A$^c$</td>
<td>T$^c$</td>
<td>A$^c$</td>
<td>T$^c$</td>
<td>A$^c$</td>
<td>T$^c$</td>
<td>A$^c$</td>
</tr>
<tr>
<td>$T_1<a href="236">\Gamma_4</a>$</td>
<td>$T_2$</td>
<td>$T_2^{(1)}$</td>
<td>$T_2$</td>
<td>$T_2$</td>
<td>T$^c$</td>
<td>E $^c$</td>
<td>E $^c$</td>
<td>T$^c$</td>
<td>E $^c$</td>
<td>T$^c$</td>
<td>E $^c$</td>
<td>T$^c$</td>
</tr>
<tr>
<td>$E<a href="422">\Gamma_3</a>$</td>
<td>E</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>T$^c$</td>
<td>T$^c$</td>
<td>T$^c$</td>
<td>T$^c$</td>
<td>T$^c$</td>
<td>T$^c$</td>
<td>T$^c$</td>
</tr>
<tr>
<td>$T_2<a href="701">\Gamma_5</a>$</td>
<td>$T_1^{(2)}$</td>
<td>$A_2[\Gamma_2]$</td>
<td>$T_2$</td>
<td>$T_2$</td>
<td>T$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
<td>A$^c$</td>
</tr>
<tr>
<td></td>
<td>$T_1$</td>
<td>$T_2^{(2)}$</td>
<td>$T_1$</td>
<td>$T_2^{(2)}$</td>
<td>$T_1$</td>
<td>$T_2^{(2)}$</td>
<td>$T_1$</td>
<td>$T_2^{(2)}$</td>
<td>$T_1$</td>
<td>$T_2^{(2)}$</td>
<td>$T_1$</td>
<td>$T_2^{(2)}$</td>
</tr>
</tbody>
</table>

$^a$ Experimental energy data in cm$^{-1}$; $^b$ 2300 cm$^{-1}$; $^c$ 4392 cm$^{-1}$ [13].
According to the procedure outlined in 3.3.2, only the ground multiplet $^3H_4$ will be considered for the 4f$^2$ ion, that is, one starts with the $|JM_J\rangle$ basis consisting of the $2J + 1 = 9$ states $|44\rangle, |43\rangle, \ldots, |4 - 4\rangle$. The 4f$^2$ situation is much more complicated than the 4f$^1$ one for the following reasons: In order to apply the entries of Table 13, the $|JM_J\rangle$ functions have to be decomposed into the microstates of the two electrons (cf. ref. [7], page 120). Subsequently, the operator eq. (88) must be applied. Then the respective LF matrix elements have to be summed up and collected in a $9 \times 9$ matrix. After diagonalisation of this matrix, the symmetry adapted functions and their energies are obtained as a function of the LF parameters $B_4^0$ and $B_6^0$.

These calculations would be time-consuming and must be worked out by a computer, using, for example, the program CONDON [12] which is at our disposal. In general, this program uses the complete set of basis functions, but can be restricted to the ground multiplet. The results, obtained by CONDON with the restricted basis, are presented in Table 18. A splitting in a singlet ($A_1$), a doublet (E) and two triplets ($T_1, T_2$) is obtained and the entries of Table 17 are confirmed.

**Tab. 18:** Functions and energies after perturbation of the $^3H_4(4f^2)$ ground multiplet by a cubic ligand field

| functions $|M_J\rangle$ ($J = 4$) | $\Gamma \bar{M}^{a)}$ | $E_{LF} \, b)$ |
|----------------------------------|----------------|----------------|
| $\sqrt{\frac{1}{24}} \left( \sqrt{\frac{11}{4}} |0\rangle + \sqrt{5} |4\rangle + \sqrt{5} |-4\rangle \right)$ | $A_1a_1$ | $28b_4 - 80b_6$ |
| $\sqrt{\frac{1}{24}} \left( -\sqrt{10} |0\rangle + \sqrt{7} |4\rangle + \sqrt{7} |-4\rangle \right)$ | $E\theta$ | $4b_4 + 64b_6$ |
| $\sqrt{\frac{1}{2}} (|2\rangle + |-2\rangle)$ | $E\epsilon$ | |
| $-\sqrt{\frac{1}{8}} |-3\rangle - \sqrt{\frac{7}{8}} |1\rangle$ | $T_{11}$ | |
| $\sqrt{\frac{1}{2}} (|4\rangle - |-4\rangle)$ | $T_{10}$ | $14b_4 + 4b_6$ |
| $\sqrt{\frac{1}{8}} |3\rangle + \sqrt{\frac{7}{8}} |-1\rangle$ | $T_{1} - 1$ | |
| $\sqrt{\frac{7}{8}} |3\rangle - \sqrt{\frac{1}{8}} |-1\rangle$ | $T_{21}$ | |
| $\sqrt{\frac{1}{2}} (|2\rangle - |-2\rangle)$ | $T_{20}$ | $-26b_4 - 20b_6$ |
| $-\sqrt{\frac{1}{8}} |-3\rangle + \sqrt{\frac{7}{8}} |1\rangle$ | $T_{2} - 1$ | |

$^a)$ $A_1 \equiv \Gamma_1, E \equiv \Gamma_3, T_1 \equiv \Gamma_4, T_2 \equiv \Gamma_5$ [6].

$^b)$ $b_4 = (15/2)\beta_J B_4^0, b_6 = (315/4)\gamma_J B_6^0; \quad \beta_J = \frac{4}{3145}, \quad \gamma_J = \frac{242}{4459455}$.

---

11) As an alternative, a rather simple method is available to determine LF effects for cubic lanthanide systems, if the description of the LF effect within the ground multiplet is sufficient. In this method an operator is applied that consists of so-called operator-equivalents instead of the Racah tensors. We will come back to its practice in 3.3.7 and in Appendix 2.
3.3.6 4f² system (Pr³⁺, ³H₄: $H_{\text{LF}}^\text{cub} + H_{\text{mag}}$)

Applying the Zeeman operator eq. (66) on the eigenfunctions, the matrix elements (89) are obtained (in units of $g_J \mu_B B_z$; $g_J = 4/5$).

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$\bar{M}$</th>
<th>$A_1$</th>
<th>$E$</th>
<th>$T_1$</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$a_1$</td>
<td>0</td>
<td>0</td>
<td>$\sqrt{\frac{20}{3}}$</td>
<td>1 0 -1</td>
</tr>
<tr>
<td>$E$</td>
<td>$\theta$</td>
<td>0</td>
<td>0</td>
<td>$\sqrt{\frac{28}{3}}$</td>
<td>0 0 0</td>
</tr>
<tr>
<td>$T_1$</td>
<td>0</td>
<td>1</td>
<td>$\sqrt{\frac{20}{3}}$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>0</td>
<td>$\sqrt{\frac{28}{3}}$</td>
<td>0</td>
<td>$-\frac{\sqrt{7}}{2}$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>$\frac{\sqrt{7}}{2}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>2</td>
<td>$\frac{\sqrt{7}}{2}$</td>
<td>$\frac{5}{2}$</td>
<td>$-\frac{5}{2}$</td>
</tr>
</tbody>
</table>

In Table 19 the energies $W^{(0)}_n$ and the Zeeman coefficients $W^{(1)}_n, W^{(2)}_n$ are listed.

**Tab. 19:** Energies $W^{(0)}_n$ and Zeeman coefficients $W^{(1)}_n, W^{(2)}_n$ of the 4f² system (Pr³⁺) after perturbation of the ³H₄ multiplet by a cubic ligand field.

| $|\psi_n \rangle$ | $W^{(0)}_n a$ | $W^{(1)}_n$ | $W^{(2)}_n$ |
|-------------------|--------------|--------------|--------------|
| $|A_1 a_1 \rangle$ | $28 b_4 - 80 b_6$ | 0 | $-\frac{(20/3)}{\Delta(T_1; A_1)}$ |
| $|E\theta\rangle$  | $4 b_4 + 64 b_6$ | 0 | $-\frac{(28/3)}{\Delta(T_1; E)}$ |
| $|E\epsilon\rangle$ | 0 | 0 | $-\frac{(7/4)}{\Delta(T_2; E)}$ |
| $|T_1 \pm 1 \rangle$ | $14 b_4 + 4 b_6$ | $\pm 1/2$ | $-\frac{(20/3)}{\Delta(T_1; T_1)} + \frac{(28/3)}{\Delta(T_2; T_1)}$ |
| $|T_1 0 \rangle$     | 0 | 0 | $+\frac{(7/4)}{\Delta(T_2; T_1)}$ |
| $|T_2 \pm 1 \rangle$ | $-26 b_4 - 20 b_6$ | $\pm 5/2$ | $\frac{28}{4} \Delta(T_2; T_1)$ |
| $|T_2 0 \rangle$     | 0 | 0 | $\frac{28}{4} \Delta(T_2; T_1)$ |

a) Further contributions to $W^{(0)}_n$ beside $E_{\text{LF}}$ are equal in magnitude for all levels and are reduced: $b_4 = (15/2) \beta J B_0^4$, $b_6 = (315/4) J B_0^6$.

b) $\Delta(\Gamma_m; \Gamma_n) = W^{(0)}_m - W^{(0)}_n$. 

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Setting $W_n^{(0)}$, $W_n^{(1)}$ and $W_n^{(2)}$ into the Van Vleck eq. (60), the susceptibility equation for the Pr$^{3+}$ ion in cubic ligand fields is developed (where $X_\Gamma \equiv W_n^{(0)}(\Gamma)/k_BT)$:

$$\chi_m(\text{Pr}^{3+}) = \mu_0 \frac{N_A \mu_B^2}{3k_BT} \mu_{\text{eff}}^2 \quad \text{where} \quad \mu_{\text{eff}}^2 = g_f^2 \times \left[ \frac{40k_BT}{\Delta(T_1; A_1)} \right] \exp(-X_{A_1}) + \left[ \frac{3}{2} + \frac{21k_BT}{\Delta(T_2; T_1)} - \frac{40k_BT}{\Delta(T_1; A_1)} - \frac{56k_BT}{\Delta(T_1; E)} \right] \exp(-X_{T_1}) + \left[ \frac{75}{2} - \frac{21k_BT}{\Delta(T_2; T_1)} - \frac{24k_BT}{\Delta(T_2; E)} \right] \exp(-X_{T_2}) \right] \times \left\{ \exp(-X_{A_1}) + 2 \exp(-X_E) + 3 \exp(-X_{T_1}) + 3 \exp(-X_{T_2}) \right\}^{-1} \tag{90}$$

Fig. 13 (left) exhibits calculated $\chi_m^{-1}T$ and $\mu_{\text{eff}}^{-1}T$ diagrams for the Pr$^{3+}$ ion in an octahedral ligand field where $B_1^0 = 1938 \text{ cm}^{-1}$ and $B_0^6 = 290 \text{ cm}^{-1}$. Dotted lines refer to calculations with the reduced basis $^3H_4$ (eq. (90)), whereas the solid lines correspond to calculations with the complete basis (91 microstates). Differences in $\chi_m$ values between the two models amount to 3%. In addition, the expected magnetic behaviour of the free ion is shown for comparison (dashed lines).

### 3.3.7 Prediction of LF splittings by means of the operator-equivalent method

The magnetic behaviour of Ln ions depends on position and charge of the ligands, both controlling sign and amount of the LF parameters $B_q^k$. If one accepts the qualitative validity of the point charge electrostatic model (PCEM) for the geometrical coordination factor $A_q^k$ (defined in eq. (72)), the sign of the corresponding $B_q^k = A_q^k < r^k >$, that is, the sign of $B_0^4$ and $B_0^6$ in the case of cubic coordination polyhedra (octahedron, cube, tetrahedron), can be predicted reliably. We consider the point charges $-Qe^{13}$ at the vertices of regular polyhedra (octahedron, tetrahedron, cube) with the distance $R$ to the centre of the polyhedron, and calculate $A_0^4$ and $A_0^6$.

#### Geometrical coordination factors

For the octahedron the integration in eq. (72) reduces to a summation of the six ligands with $(\Theta_j, \Phi_j)$ coordinates $(0, 0), (\pi, 0), (\pi/2, 0), (\pi/2, \pi/2), (\pi/2, \pi), (\pi/2, 3\pi/2)$:

$$A_0^4(\text{oct.}) = \frac{Qe^2}{R^5} \sum_{j=1}^{6} C_4^4(\Theta_j, \Phi_j) = \frac{Qe^2}{R^5} \sum_{j=1}^{6} \frac{1}{8} (35 \cos^4 \Theta_j - 30 \cos^2 \Theta_j + 3) = \frac{7 Qe^2}{2 R^5}, \tag{91}$$

For negatively charged ligands ($Q > 0$) which coordinate the Ln ion octahedrally, $A_0^4(\text{oct.})$ is positive and consequently also $A_0^4 < r^4 > = B_0^4$, whereas the $A_0^q$‘s for tetrahedron and cube are negative (angle coordinates for tetrahedron: $(\alpha, \pi/4), (\alpha, 5\pi/4), (\pi - \alpha, 3\pi/4)$).

---

12) Notice, that radial integrals $< r^k >$ are positive quantities.

13) The elementary charge $e$ is positive; the charge of the electron is $-e$. Ligands with the charge $-Qe$ are negatively charged for $Q > 0$. 
\[ (\pi - \alpha, 7\pi/4), \text{ where } \cos \alpha = 1/\sqrt{3}; \text{ additionally for the cube } (\alpha, 3\pi/4), (\alpha, 7\pi/4), (\pi - \alpha, \pi/4), (\pi - \alpha, 5\pi/4)\]:

\[ A_i^0(\text{tetra}) = -\frac{14}{9} \frac{Q_e^2}{R^5}; \quad A_i^0(\text{cube}) = \frac{28}{9} \frac{Q_e^2}{R^5} \quad (92) \]

\[ A_6^0 \]

\[ A_6^0(\text{oct}) = \frac{Q_e^2}{R^7} \sum_{j=1}^{6} C_6^0(\Theta_j, \Phi_j), \quad \text{where} \quad C_6^0(\Theta_j, \Phi_j) = \left(\frac{4\pi}{13}\right)^{1/2} Y_6^0(\Theta_j, \Phi_j) \]

\[ = \frac{Q_e^2}{R^7} \sum_{j=1}^{6} \frac{1}{16}(231 \cos^6 \Theta_j - 315 \cos^4 \Theta_j + 105 \cos^2 \Theta_j - 5) = \frac{3}{4} \frac{Q_e^2}{R^7} \quad (93) \]

\[ A_6^0(\text{tetra}) = \frac{8}{9} \frac{Q_e^2}{R^7}; \quad A_6^0(\text{cube}) = \frac{16}{9} \frac{Q_e^2}{R^7} \quad (94) \]

For negatively charged ligands \((Q > 0)\), \(A_i^0\) is positive, regardless the polyhedron.

Having fixed the sign of the LF parameters \(B_3^0\) and \(B_6^0\), the possible LF ground states of the Ln ion under investigation can be determined. If the program CONDON is at our disposal, we need only the values of \(B_3^0\) and \(B_6^0\) as an input to obtain energy and composition of the LF states. Otherwise, we can benefit from tables of eigenvectors and diagrams of energy eigenvalues, expressed as a function of the ratio between the fourth and sixth degree terms of \(\hat{H}_{\text{LF}}^{\text{cub}}\), that are published for all \(J\)-manifolds of the lanthanides by Lea, Leask, Wolf [16]. The immediate application of these diagrams and tables is the prediction of spectroscopic energy level schemes and possible \(g\)-factors for lanthanide ions in cubic coordination. We start with introductory remarks concerning the operator equivalent technique.

**Operator equivalents:** To describe the fundamental magnetic behaviour of Ln ions in a solid, a model is sufficient that, according to the Russell-Saunders coupling scheme, takes solely the ground multiplet \(2S+1L_J\) and its perturbation by \(\hat{H}_{\text{LF}}\) into consideration (exceptions: \(\text{Sm}^{3+}[4f^5]\), \(\text{Eu}^{3+}[4f^6]\)). The restriction of the basis functions allows a simple calculation of the matrix elements \(\langle J M_J | \hat{H}_{\text{LF}} | J M'_J \rangle\) by application of the so-called operator-equivalent technique. Using this technique, the calculation of the integrals \(\langle l_i m_{l_i} | C_q^k(i) | l_j m_{l_j} \rangle\) — entailing a troublesome decoding of the \(| J M_J \rangle\) basis with regard to the microstates — is unnecessary.

The operator equivalent technique is founded on the fact that the operators \(C_q^k = \sqrt{4\pi/(2k+1)} Y_q^k\), written in cartesian coordinates, can be replaced by operators \(\hat{J}_x, \hat{J}_y, \hat{J}_z\) of the total angular momentum [17] [14]. By this means operator equivalents \(\tilde{O}_q^k\) are designed whose matrix elements are proportional to the corresponding matrix elements of \(\hat{H}_{\text{LF}}\). The restriction to the ground multiplet has the advantage that the matrix elements \(\langle J M_J | \hat{H}_{\text{LF}}^{\text{cub}} | J M'_J \rangle\) are easily evaluated: Given the wave functions in the \(| J M_J \rangle\) basis, the action of \(\hat{H}_{\text{LF}}^{\text{cub}}\) on the orbital part of the functions is taken into consideration by a simple factor (Stevens factor [18]). If \(x, y, z\) in the Racah tensors \(C_q^k(x, y, z)\) of \(\hat{H}_{\text{LF}}^{\text{cub}}\) (eq. (72)) are replaced by the total angular momentum operators \(\hat{J}_x, \hat{J}_y, \hat{J}_z\) [17], operator equivalents

\[ \text{Conversion factors are published in ref. [22]. Details are given in the 'Final remarks', p. 49.} \]
$\tilde{O}_k^n$ are obtained, whose matrix elements are proportional to the matrix elements of $\hat{H}_L^{\text{cub}}$. Simple examples of operator equivalents are:

\[
x^2 - y^2 \equiv \theta(\hat{J}_x^2 - \hat{J}_y^2), \quad 3z^2 - r^2 \equiv \theta[3\hat{J}_z^2 - J(J+1)], \quad xy \equiv \theta(\frac{1}{2})(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x).
\]

The multiplicative (Stevens) factor $\theta$ depends on $k$:

\[
\alpha_J \quad (k = 2) \quad \beta_J \quad (k = 4) \quad \gamma_J \quad (k = 6)
\]

(see Table 23 and example 3.8)

For cubic symmetry only terms with $k = 4$ and 6 are relevant, so that the multiplet under consideration is generally characterised by the two figures $\beta_J$ and $\gamma_J$. The two following equations show the operator and its operator equivalent:

\[
\hat{H}_L^{\text{cub}}(4f^N) = B_0^4 \sum_{i=1}^{N} \left\{ C_0^4(i) + \sqrt{\frac{5}{14}} [C_4^4(i) + C_{-4}^4(i)] \right\} + B_0^6 \sum_{i=1}^{N} \left\{ C_0^6(i) - \sqrt{\frac{7}{2}} [C_4^6(i) + C_{-4}^6(i)] \right\}
\]

\[
\hat{H}_L^{\text{cub}} = B_0^4 \beta_J \left[ \tilde{O}_4^0 + \sqrt{\frac{5}{14}} \left( \tilde{O}_4^4 + \tilde{O}_{-4}^4 \right) \right] + B_0^6 \gamma_J \left[ \tilde{O}_4^6 - \sqrt{\frac{7}{2}} \left( \tilde{O}_4^6 + \tilde{O}_{-4}^6 \right) \right]
\]

(95)

The operators $C_q^4$ and $\tilde{O}_q^4$ as well as $C_q^6$ and $\tilde{O}_q^6$ are related (see ref. [17]) by

\[
\sum_{i=1}^{N} C_0^4(i) = \beta_J \tilde{O}_0^4 = \beta_J \left( \frac{1}{8} \right) \left\{ 35\hat{J}_z - [30J(J+1) - 25]\hat{J}_z^2 + 3J^2(J+1)^2 - 6J(J+1) \right\}
\]

\[
\sum_{i=1}^{N} C_{\pm 4}^4(i) = \beta_J \tilde{O}_{\pm 4}^4 = \beta_J \left( \frac{1}{8} \right) \sqrt{70} \left( \frac{3}{7} \right) \hat{J}_z^4
\]

(96)

\[
\sum_{i=1}^{N} C_0^6(i) = \gamma_J \tilde{O}_0^6 = \gamma_J \left( \frac{1}{16} \right) \left\{ 231\hat{J}_z - [315J(J+1) - 735]\hat{J}_z^2 + [105J^2(J+1)^2 - 525J(J+1) + 294]\hat{J}_z^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1) \right\}
\]

\[
\sum_{i=1}^{N} C_{\pm 4}^6(i) = \gamma_J \tilde{O}_{\pm 4}^6 = \gamma_J \sqrt{\frac{63}{128}} \left( \frac{1}{8} \right) \left\{ [11\hat{J}_z^2 - J(J+1) - 38]\hat{J}_z^4 + \hat{J}_z^4 + \hat{J}_z^4 \right\}
\]

(97)

The matrix elements $\langle JM_J | \tilde{O}_q^k | JM'_J \rangle$ that are necessary to set up $H_L^{\text{cub}}$ matrices are available and collected in the Tables 35 – 38 on pages 89 – 90. In the following three examples the handling of operator equivalents is shown.

**Example 3.7 Application of the operator-equivalent method to $^2F_{5/2}$ of Ce$^{3+}[4f^1]$**

The $H_L^{\text{cub}}$ operator equivalent for the cubic $4f^1$ system reads

\[
\hat{H}_L^{\text{cub}} = B_0^4 \beta_J \left[ \tilde{O}_0^4 + \sqrt{\frac{5}{14}} \left( \tilde{O}_4^4 + \tilde{O}_{-4}^4 \right) \right]
\]

(98)

Inspecting the Tables 35 and 36 the relevant data for the basis $|\frac{5}{2} M_J \rangle$ are:

\[
\begin{align*}
\langle \pm \frac{1}{2} | \tilde{O}_0^4 \pm \frac{1}{2} \rangle &= 15, & \langle \pm \frac{5}{2} | \tilde{O}_0^4 \pm \frac{5}{2} \rangle &= 15/2, \\
\langle \pm \frac{3}{2} | \tilde{O}_0^4 \pm \frac{3}{2} \rangle &= -45/2, & \langle \pm \frac{7}{2} | \tilde{O}_{\pm 4}^4 \pm \frac{7}{2} \rangle &= 15\sqrt{14}/2.
\end{align*}
\]

(99)

\footnote{Exceptions are the multiplets $^2F_{5/2}$ (Ce$^{3+}[4f^1]$) and $^6H_{5/2}$ (Sm$^{3+}[4f^5]$) with $J = 5/2$, where only the fourth degree term ($k = 4$) in $\hat{H}_L^{\text{cub}}$ is relevant.}
Example 3.8 Evaluation of $\beta \gamma \times$ and three $2^k$

Evaluation of the $\hat{b}$ where

\[
\langle V \text{erification of} \rangle \text{On the basis of the operator-equivalent matrix elements (99) and}
\]

Notice that, applying operator equivalents, the factor $\hbar$ is always omitted.

To complete the matrix elements they must be multiplied by $\beta_J = \frac{2}{315}$ (see Table 23). Example 3.8 shows the evaluation of the Stevens factor $\beta_J$.

**Example 3.8 Evaluation of $\beta_J$ for $^3F_{5/2}$ [4f$^1$]**

$\beta_J$ is derived by comparing $\langle \frac{5}{2} \mid C^4 \mid \frac{5}{2} \rangle$ (Example 3.5) with $\langle \frac{5}{2} \mid \hat{O}_0^4 \mid \frac{5}{2} \rangle$ (Example 3.7):

\[
\langle \frac{5}{2} \mid C^4 \mid \frac{5}{2} \rangle_{1/21} = \beta_J \langle \frac{5}{2} \mid \hat{O}_0^4 \mid \frac{5}{2} \rangle_{15/2} \quad \longrightarrow \quad \beta_J = \frac{2}{3^2 \cdot 5 \cdot 7} = \frac{2}{315}
\]

On the basis of the operator-equivalent matrix elements (99) and $\beta_J = \frac{2}{315}$ (Example 3.8) the $\hat{H}^\text{cub}_{\text{LF}}$ matrix within the basis $^2F_{5/2}$ can be set up. It is identical to matrix (83).

**Example 3.9 Application of the operator-equivalent method to Pr$^{3+}$[4f$^2$], $^3H_4$, $J = 4$**

For the 4f$^2$ system both the fourth and the sixth degree terms of the LF operator equivalents eq. (95) have to be applied. According to the 1st column in Table 17, the 9-fold degenerate ground multiplet $^3H_4$ decomposes under the action of a cubic LF into the terms $A_1$, E, $T_1$, and $T_2$. In order to verify the splitting by use of the operator-equivalent method, we need the matrix elements $\langle M_J \mid \hat{O}_0^k \mid M_J \rangle$ and $\langle M_J \mid \hat{O}_+^k \mid M_J \mp 4 \rangle$ for $k = 4$ and $k = 6$ (Table 20 and Tables 35 – 38 in Appendix 2) as well as $\beta_J = -(4/5445)$ and $\gamma_J = (272/4459455)$, given in Table 23. The $9 \times 9$ matrix is divided into one $3 \times 3$ block and three $2 \times 2$ blocks:

|   | $|4\rangle$ | $|0\rangle$ | $|-4\rangle$ |
|---|---|---|---|
| $\langle 4|$ | $14b_4 + 4b_6$ | $\sqrt{70} \ (b_4 - 6b_6)$ | $0$ |
| $\langle 0|$ | $\sqrt{70} \ (b_4 - 6b_6)$ | $18b_4 - 20b_6$ | $\sqrt{70} \ (b_4 - 6b_6)$ |
| $\langle -4|$ | $0$ | $\sqrt{70} \ (b_4 - 6b_6)$ | $14b_4 + 4b_6$ |

where $b_4 = (\frac{15}{2})\beta_J B_0^4$, and $b_6 = (\frac{315}{4})\gamma_J B_0^6$ (100)

|   | $|\pm 3\rangle$ | $|\mp 1\rangle$ | $|2\rangle$ | $|-2\rangle$ |
|---|---|---|---|---|
| $\langle \pm 3|$ | $-21b_4 - 17b_6$ | $\sqrt{7} \ (5b_4 + 3b_6)$ | $2b_4$ | $0$ |
| $\langle \mp 1|$ | $\sqrt{7} \ (5b_4 + 3b_6)$ | $11b_4 + b_6$ | $-11b_4 + 22b_6$ | $15b_4 + 42b_6$ |
| $\langle 2|$ | $-11b_4 + 22b_6$ | $15b_4 + 42b_6$ | $-11b_4 + 22b_6$ |

Evaluation of the $\hat{H}^\text{cub}_{\text{LF}}$ matrix yields the energies and eigenfunctions given in Table 21. The splitting in a singlet ($A_1$), a doublet (E) and two triplets ($T_1, T_2$) is confirmed.
The ground state of an Ln ion in a cubic LF depends on the ratio \( \beta \). We start out from eq. (95) in order to keep the energy values in the same numerical range for all ratios of the LF states as a function of the LF states in the basis \(|JM_J\rangle (J = 4 \text{ for } 4f^2 \text{ and cubic symmetry (see Appendix 2)})

| \langle M_J|\tilde{O}_q^k|M_{J'}\rangle | k = 4 | k = 6 | \langle M_J|\tilde{O}_q^k|M_{J'}\rangle | k = 4 | k = 6 |
|----------------|--------|-------|----------------|--------|-------|
| \langle 0|\tilde{O}_0^k|0\rangle | 135 | -1575 | \langle \pm 4|\tilde{O}_0^k|\pm 4\rangle | 105 | 315 |
| \langle \pm 1|\tilde{O}_0^k|\pm 1\rangle | \frac{135}{2} | \frac{315}{4} | \langle \pm 2|\tilde{O}_{\pm 4}^k|\mp 2\rangle | \frac{45}{2}\sqrt{70} | -\frac{945}{2}\sqrt{14} |
| \langle \pm 2|\tilde{O}_0^k|\pm 2\rangle | -\frac{165}{2} | \frac{3465}{2} | \langle \pm 3|\tilde{O}_{\pm 4}^k|\mp 1\rangle | \frac{105}{2}\sqrt{35} | -\frac{945}{4}\sqrt{2} |
| \langle \pm 3|\tilde{O}_0^k|\pm 3\rangle | -\frac{315}{2} | -\frac{5355}{4} | \langle \pm 4|\tilde{O}_{\pm 4}^k|0\rangle | 105 | 945\sqrt{5} |

Tab. 20: Matrix elements of the operator equivalents \( \tilde{O}_q^k \) in the basis \(|JM_J\rangle (J = 4 \text{ for } 4f^2 \text{ and cubic symmetry (see Appendix 2)})

Tab. 21: Functions and energies after perturbation of the \( ^3H_4(4f^2) \) multiplet by a cubic ligand field

| functions \(|M_J\rangle (J = 4)\) | \langle \Gamma M\rangle a)\rangle | E_{LF} b) |
|----------------|----------------|----------|
| \sqrt{\frac{1}{31}} (\sqrt{14}|0\rangle + \sqrt{5}|4\rangle + \sqrt{5}|4\rangle - \sqrt{4} \rangle) | \langle A_1a_1 \rangle | 28b_4 - 80b_6 |
| \sqrt{\frac{1}{31}} (\sqrt{10}|0\rangle + \sqrt{7}|4\rangle + \sqrt{7}|4\rangle - \sqrt{4} \rangle) | \langle E\theta \rangle | 4b_4 + 64b_6 |
| \sqrt{\frac{1}{5}} (|2\rangle + |1\rangle - |2\rangle - |1\rangle) | \langle 1T_0 \rangle | 14b_4 + 4b_6 |
| \sqrt{\frac{1}{3}} (|3\rangle + \sqrt{\frac{2}{8}}|1\rangle - |3\rangle - \sqrt{\frac{2}{8}}|1\rangle) | \langle 1T_0 \rangle | 26b_4 - 20b_6 |
| \sqrt{\frac{1}{3}} (|3\rangle - \sqrt{\frac{1}{8}}|1\rangle - |3\rangle + \sqrt{\frac{1}{8}}|1\rangle) | \langle 1T_1 \rangle | -26b_4 - 20b_6 |
| \sqrt{\frac{1}{3}} (|2\rangle + |1\rangle - |2\rangle - |1\rangle) | \langle 1T_2 \rangle | -26b_4 - 20b_6 |
| \sqrt{\frac{1}{3}} (|2\rangle - |1\rangle - |2\rangle + |1\rangle) | \langle 1T_2 \rangle | -26b_4 - 20b_6 |

a) Assignment of the states see ref. [6]: \( A_1 \equiv \Gamma_1, E \equiv \Gamma_3, T_1 \equiv \Gamma_4, T_2 \equiv \Gamma_5 \).

b) \( b_4 = (15/2)\beta_JB_0^4, b_6 = (315/4)\gamma_JB_0^6 \).

Level tuning [16]: The ground state of an Ln ion in a cubic LF depends on \( \beta_JB_0^4 \) and \( \gamma_JB_0^6 \). We want to obtain information about the succession of \( E_{LF} \) of the LF states as a function of the ratio \( \beta_JB_0^4/\gamma_JB_0^6 \). Using the operator equivalent matrix elements in Tables 35 – 38, the \((2J + 1) \times (2J + 1) \) matrix can in principle be drawn up. The tables contain factors common to all the matrix elements, \( \tilde{F}(4) \) and \( \tilde{F}(6) \). These factors are separated out in order to keep the energy values in the same numerical range for all ratios of the fourth and sixth degree terms. We start out from eq. (95)

\[
\tilde{H}_{LF}^{\text{cub}} = \beta_JB_0^4 \left[ \tilde{O}_0^4 + \sqrt{\frac{5}{14}} \left( \tilde{O}_4^4 + \tilde{O}_4^{-4} \right) \right] + \gamma_JB_0^6 \left[ \tilde{O}_0^6 - \sqrt{\frac{7}{2}} \left( \tilde{O}_4^6 + \tilde{O}_4^{-6} \right) \right]
\]
\[
\begin{align*}
\beta J B_0^4 \hat{O}^4 + \gamma J B_0^6 \hat{O}^6 \\
= \beta J B_0^4 \bar{F}(4) \hat{O}^4 + \gamma J B_0^6 \bar{F}(6) \hat{O}^6 .
\end{align*}
\]  

(101)

In order to cover all possible values of the ratio between the fourth and sixth degree terms a mixing parameter \( x \) has been introduced which is governed by the relative magnitude of \( B_0^4 \) and \( B_0^6 \). Furthermore, a factor \( W \) has been defined that scales \( E_{\text{LF}} \):

\[
\begin{align*}
\beta J B_0^4 \bar{F}(4) = W x, \\
\gamma J B_0^6 \bar{F}(6) = W (1 - |x|) \quad \text{where} \quad -1 < x < +1
\end{align*}
\]

(102)

Solving both eqs. (102) for \( W \), an equation is obtained that covers all possible values of the ratio between \( B_0^4 \) and \( B_0^6 \). It follows that

\[
\frac{\beta J B_0^4}{\gamma J B_0^6} = \frac{x}{1 - |x|} \frac{\bar{F}(6)}{\bar{F}(4)},
\]

(103)

so that \((\beta J B_0^4/\gamma J B_0^6) = 0 \) for \( x = 0 \), while \((\beta J B_0^4/\gamma J B_0^6) = \pm \infty \) for \( x = \pm 1 \). In consequence, eq. (101) can be rewritten as

\[
\hat{H}_{\text{cub}}^{\text{LF}} = W \left[ x \left( \frac{\hat{O}^4}{\bar{F}(4)} \right) + (1 - |x|) \left( \frac{\hat{O}^6}{\bar{F}(6)} \right) \right]
\]

(104)

For each \( J \)-manifold \( x \) is allowed to take the values in the range \( 0 \to \pm 1 \). The energy expressions for the LF states as a function of \( \beta J B_0^4 \bar{F}(4) = b_4 \) and \( \gamma J B_0^6 \bar{F}(4) = b_6 \) are replaced by \( W x \) and \( W (1 - |x|) \), respectively. Table 22 exhibits the results for the \( 4f^2 \) system and Fig. 15 displays the corresponding diagram \( E_{\text{LF}}/W \) versus \( x \).

**Tab. 22:** Energies \( E_{\text{LF}} \) of the \( 4f^2 \) system in cubic ligand fields as a function of \( W \) and \( x \) as well as \( b_4 \) and \( b_6 \), see eqs. (102)

<table>
<thead>
<tr>
<th>( E_{\text{LF}} )</th>
<th>( E_{\text{LF}}/W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0 ) ( x = \pm 1 )</td>
<td></td>
</tr>
<tr>
<td>( A_1 )</td>
<td>28 ( b_4 - 80 b_6 )</td>
</tr>
<tr>
<td>( E )</td>
<td>( 4 b_4 + 64 b_6 )</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>( 14 b_4 + 4 b_6 )</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>(-26 b_4 - 20 b_6 )</td>
</tr>
</tbody>
</table>

Diagrams like Figs. 15 and 16, displaying LF energy eigenvalues \( E_{\text{LF}}/W \) as a function of the LF parameters, are available for all \( J \)-manifolds of the lanthanides’ ground multiplets [16]. In examples 3.10 and 3.11 the diagrams are used to determine the LF ground state for \( \text{Pr}^{3+}[4f^2] \) and \( \text{Nd}^{3+}[4f^3] \) in cubic LF. In example 3.12 the construction of the \( x - E_{\text{LF}}/W \) diagram for \( \text{Pr}^{3+} \) is demonstrated.
**Example 3.10 Ground state of Pr$^{3+}$ in cubic LF**

**Pr$^{3+}$: The signs of $W$ and $x$ for an octahedral LF:**

(i) The PCEM predicts that for an octahedral LF both geometrical parameters, $A_0^4$ and $A_0^6$, are positive (see eqs. (91) and (93)) and, consequently, also $B_0^4$ and $B_0^6$.

(ii) Since both $\tilde{F}(4)$ and $\tilde{F}(6)$ are positive (for all $J$'s), it is obvious from the right eq. (102) that the sign of $W$ is determined by the sign of $\gamma_J B_0^6$, since $(1 - |x|)$ is always positive for $-1 < x < +1$.

(iii) From eq. (103) we see that the sign of $x$ is determined by the sign of $(\beta_J B_0^4 / \gamma_J B_0^6)$. For the Pr$^{3+}$ system under investigation, $\gamma_J$, $B_0^4$, and $B_0^6$ are positive, while $\beta_J$ is negative (see Table 23). So, the sign of $x$ is negative.

The $x$-$E_{LF}/W$ diagram in Fig. 15 shows that for the situation $x < 0$ and $W > 0$ the singlet $A_1$ is the ground state. Thus, an octahedrally coordinated Pr$^{3+}$ ion should exhibit temperature-independent paramagnetism at low temperature. Fig. 13 (left) confirms this magnetic behaviour.

**Pr$^{3+}$: The signs of $W$ and $x$ for a tetrahedral/cubical LF:**

Since $A_0^4$ ($B_0^4$) is negative, $x$ is positive; the sign of $W$ doesn’t change compared to the octahedral case. Consequently, both $W$ and $x$ are positive and the LF ground state may be a singlet ($A_1$) or a triplet ($T_2$), depending on the magnitude of $x$ (see the region $x > 0$ in Fig. 15).

**Example 3.11 Ground state of Nd$^{3+}$[4f$^3$] in cubic LF**

**Nd$^{3+}$: The signs of $W$ and $x$ for an octahedral LF:**

(i) Applying the PCEM, the situation is identical to the Pr$^{3+}$ case: $B_0^4$, $B_0^6 > 0$.

(ii) Since $\gamma_J$ is negative, it is obvious from the right eq. (102) that $W < 0$.

(iii) From eq. (103) we see that the sign of $x$ is determined by the sign of $(\beta_J B_0^4 / \gamma_J B_0^6)$. For the Nd$^{3+}$ system under investigation both $\beta_J$ and $\gamma_J$ are negative (see Table 23). So, the sign of $x$ is positive.

---

16) The result of the PCEM calculation is supported by spectroscopic investigations, showing that $B_0^4 = 1938 \text{ cm}^{-1}$ and $B_0^6 = 290 \text{ cm}^{-1}$ (see Table 16).

17) $B_0^4 = 1966 \text{ cm}^{-1}$, $B_0^6 = 258 \text{ cm}^{-1}$ (see Table 16).
The \(x-(E_{LF}/W)\) diagram in Fig. 16 shows that for the situation \(x > 0\) and \(W < 0^{18}\) either the quartet \(G'\) or the doublet \(E'\) is the ground state. Thus, ignoring interionic spin-spin couplings, an octahedrally coordinated \(\text{Nd}^{3+}\) ion should exhibit Curie paramagnetism regardless \(T\). Fig. 13 (right) exhibits the magnetic behaviour.

Note, that the diagrams in Figs. 15 and 16 differ distinctly: While for the \(\text{Pr}^{3+}\) ion exclusively straight lines result, one straight line and two curves are observed for the \(\text{Nd}^{3+}\) ion (see 'Remarks' on page 49 for further details).

**Nd\(^{3+}\): The signs of \(W\) and \(x\) for a tetrahedral/cubical LF:**

Since both \(W\) and \(x\) are negative (according to \(\beta_J, \gamma_J, B_{4}^{0} < 0\) and \(B_{6}^{0} > 0\), eq. (103)) the ground state is the quartet \(G'\).

**Final remarks**

- According to today’s standard practice, we use the operator equivalents that are related to the Racah tensors \(C_{k}^{j}\) [17] while Stevens’ definition relates to the spherical harmonics \(Y_{k}^{j}\) [18, 19]. Since the article of Lea, Leask, Wolf [16] is based on Stevens’ definition \(Y_{k}^{j}\), some hints to the conversion factors between both derivations is informative with respect to the application of the LLW diagrams:

  1. The LLW diagrams can be applied directly, since the conversion factor for both \(W\) and \(x\) is 1. In other words, the values \(O_{4}/F(4)\) (based on \(Y_{k}^{j}\)) in equation (5) of ref. [16] and \(\tilde{O}/F(4)\) (based on \(C_{k}^{j}\)) in eq. (104) are identical and the same is true for the sixth degree terms \((k = 6)\).

  2. Conversion factors for operator equivalents (see eq. (96) and (97)):

\[
\tilde{O}_{4}^{0} = \left(\frac{1}{8}\right) O_{4}^{0}, \quad \tilde{O}_{4}^{1} = \left(\sqrt{70}/8\right) O_{4}^{1}, \quad \tilde{O}_{6}^{0} = \left(\frac{1}{16}\right) O_{6}^{0}, \quad \tilde{O}_{6}^{6} = \sqrt{63}/128 O_{6}^{6}
\]

Consequence of the conversion factors:

Conversion of \(F(4)\) and \(F(6)\) [21] into \(\tilde{F}(4)\) and \(\tilde{F}(6)\) (Table 23), respectively:

\[
\tilde{F}(4) = \left(\frac{1}{8}\right) F(4), \quad \tilde{F}(6) = \left(\frac{1}{16}\right) F(6)
\]

  3. The LF parameters, used by LLW, \(B_{4}^{0(\text{LLW})}\) and \(B_{6}^{0(\text{LLW})}\) [16], include the Stevens factors \(\beta_J\) and \(\gamma_J\), while in today’s standard practice, used by us, both are separated:

\[
B_{4}^{0(\text{LLW})} = \beta_J B_{4}^{0}, \quad B_{6}^{0(\text{LLW})} = \gamma_J B_{6}^{0}
\]

- Within the \(x-(E_{LF}/W)\) diagrams there are two types of \(\Gamma_i\) curves to be considered:

  1. A state \(\Gamma_i\) whose energy eigenvalue is a linear function of \(x\), occurs once only in the decomposition of the \(J\)-manifold. For example, in the cubic \(\text{Pr}^{3+}\) systems with ground multiplet \(J = 4\) each split term \(A_{1}(\Gamma_1), E(\Gamma_3), T_{1}(\Gamma_4), T_{2}(\Gamma_5)\) occurs once only. So, the diagram exhibits only straight lines. The state functions have fixed compositions (see Table 21) independent of \(B_{4}^{0}\) and \(B_{6}^{0}\). Other examples are ions in cubic LF’s with \(J = \frac{5}{2}\) (\(E''(\Gamma_7), G'(\Gamma_8)\)) and \(\frac{7}{2}\) (\(E'(\Gamma_6), E''(\Gamma_7), G'(\Gamma_8)\)).

---

\(^{18}\) According to the negative sign of \(W\), one has to mirror the \(x-(E_{LF}/W)\) diagram at the \(x\) axis with the consequence that the \(E_{LF}/W\) axis shows downwards for \(W < 0\).
Tab. 23: Ground states of Ln$^{3+}$ ions in cubic ligand fields [16]

<table>
<thead>
<tr>
<th>Ln$^{3+}$[4f$^N$]</th>
<th>Ce$^{3+}$[4f$^1$]</th>
<th>Pr$^{3+}$[4f$^2$]</th>
<th>Nd$^{3+}$[4f$^3$]</th>
<th>Sm$^{3+}$[4f$^5$]</th>
<th>Tb$^{3+}$[4f$^8$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2S+1L_J$</td>
<td>$2F_{5/2}$</td>
<td>$3H_4$</td>
<td>$4I_{9/2}$</td>
<td>$6H_{5/2}$</td>
<td>$7F_6$</td>
</tr>
<tr>
<td>$\alpha_J$</td>
<td>$-2/35$</td>
<td>$-52/2475$</td>
<td>$-7/1089$</td>
<td>$13/315$</td>
<td>$-1/99$</td>
</tr>
<tr>
<td>$\beta_J$</td>
<td>$2/315$</td>
<td>$-4/5445$</td>
<td>$-136/467181$</td>
<td>$26/10395$</td>
<td>$2/16335$</td>
</tr>
<tr>
<td>$\gamma_J$</td>
<td>0</td>
<td>$272/4459455$</td>
<td>$-1615/42513471$</td>
<td>0</td>
<td>$-1/891891$</td>
</tr>
<tr>
<td>$\bar{F}(4)^{a)}$</td>
<td>$15/2$</td>
<td>$15/2$</td>
<td>$21/2$</td>
<td>$15/2$</td>
<td>$15/2$</td>
</tr>
<tr>
<td>$\bar{F}(6)$</td>
<td>0</td>
<td>$315/4$ b)</td>
<td>$315$</td>
<td>0</td>
<td>$945/2$</td>
</tr>
<tr>
<td>$\Gamma^{[O]}c)$</td>
<td>$E''[\frac{1}{\Gamma_{\beta}}]$ d)</td>
<td>A$<em>1[\frac{1}{\Gamma</em>{\alpha}}]$</td>
<td>G$'$, E$'$ $[\frac{1}{\Gamma_{\gamma}}]$</td>
<td>E$''[\frac{1}{\Gamma_{\theta}}]$</td>
<td>A$_2$, A$<em>1[\frac{1}{\Gamma</em>{\delta}}]$</td>
</tr>
<tr>
<td>$\Gamma^{[T]}$</td>
<td>$G'[\frac{1}{\Gamma_{\delta}}]$</td>
<td>A$_1$, T$<em>2[\frac{1}{\Gamma</em>{\alpha}}]$</td>
<td>G$'$ $[\frac{1}{\Gamma_{\alpha}}]$</td>
<td>G$'[\frac{1}{\Gamma_{\theta}}]$</td>
<td>A$<em>2$, E $[\frac{1}{\Gamma</em>{\delta}}]$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ln$^{3+}$[4f$^N$]</th>
<th>Dy$^{3+}$[4f$^9$]</th>
<th>Ho$^{3+}$[4f$^{10}$]</th>
<th>Er$^{3+}$[4f$^{11}$]</th>
<th>Tm$^{3+}$[4f$^{12}$]</th>
<th>Yb$^{3+}$[4f$^{13}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2S+1L_J$</td>
<td>$6H_{15/2}$</td>
<td>$5I_8$</td>
<td>$4I_{15/2}$</td>
<td>$3H_6$</td>
<td>$2F_{7/2}$</td>
</tr>
<tr>
<td>$\alpha_J$</td>
<td>$-2/315$</td>
<td>$-1/450$</td>
<td>$4/1575$</td>
<td>$1/99$</td>
<td>$2/63$</td>
</tr>
<tr>
<td>$\beta_J$</td>
<td>$-8/135135$</td>
<td>$-1/30030$</td>
<td>$2/45045$</td>
<td>$8/49005$</td>
<td>$-2/1155$</td>
</tr>
<tr>
<td>$\gamma_J$</td>
<td>$4/3864861$</td>
<td>$-5/3864861$</td>
<td>$8/3864861$</td>
<td>$-5/891891$</td>
<td>$4/27027$</td>
</tr>
<tr>
<td>$\bar{F}(4)$</td>
<td>$15/2$</td>
<td>$105/2$</td>
<td>$15/2$</td>
<td>$15/2$</td>
<td>$15/2$</td>
</tr>
<tr>
<td>$\bar{F}(6)$</td>
<td>$3465/4$</td>
<td>$3465/4$</td>
<td>$3465/4$</td>
<td>$945/2$</td>
<td>$315/4$ b)</td>
</tr>
<tr>
<td>$\Gamma^{[O]}$</td>
<td>$E''$, E$'$ $[\frac{1}{\Gamma_{\beta}}]$</td>
<td>E$<em>1[\frac{1}{\Gamma</em>{\alpha}}]$</td>
<td>E$''$, G$'$ $[\frac{1}{\Gamma_{\gamma}}]$</td>
<td>A$_2$, A$<em>1[\frac{1}{\Gamma</em>{\delta}}]$</td>
<td>E$'$ $[\frac{1}{\Gamma_{\delta}}]$</td>
</tr>
<tr>
<td>$\Gamma^{[T]}$</td>
<td>$E''$, G$'$ $[\frac{1}{\Gamma_{\delta}}]$</td>
<td>E$_1$, T$<em>2[\frac{1}{\Gamma</em>{\alpha}}]$</td>
<td>E$''$, E$'$ $[\frac{1}{\Gamma_{\gamma}}]$</td>
<td>A$<em>2$, E $[\frac{1}{\Gamma</em>{\delta}}]$</td>
<td>E$'$, E$''$ $[\frac{1}{\Gamma_{\delta}}]$</td>
</tr>
</tbody>
</table>

$a)$ $\bar{F}(4)$ and $\bar{F}(6)$ are equivalent to $F(4)$ and $F(6)$ [16] and consider the different definitions of the operator equivalents $O^a_{\alpha}$ and $O^a_{\theta}$.

$b)$ Note that there is a misprint in the corresponding Table 4.39 of ref. [7].

$c)$ Indices $O$ and $T$ identify the expected LF ground state for octahedral and tetrahedral (cubical) symmetry and negatively charged ligands ($A_1 \equiv \Gamma_1$; $A_2 \equiv \Gamma_2$; $E \equiv \Gamma_3$; $T_1 \equiv \Gamma_4$; $T_2 \equiv \Gamma_5$; $E' \equiv \Gamma_6$; $E'' \equiv \Gamma_7$; $G' \equiv \Gamma_8$).

$d)$ Combination of signs for the W and x parameter $[\frac{W}{x}]$.

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(ii) Systems with \( J > 4 \) decompose as well into states which occur more than once and deviate from straight lines. Taking \( J = \frac{9}{2} \) (Nd\(^{3+}\)) as an example, decomposition by \( H_{LF}^{\text{cub}} \) takes place into the states \( E'(\Gamma_6) \), \( G'(\Gamma^{(1)}_8) \), \( G''(\Gamma^{(2)}_8) \). Here the energy of the states \( G'(\Gamma^{(1)}_8) \) and \( G''(\Gamma^{(2)}_8) \) depends in a more complicated way on the ratio \( B^4_0/B^6_0 \) and consequently on \( x \) (see Fig. 16\(^{19}\)). This is the consequence of the fact that the functions of both states transform according to the same irreducible representation of the cubic group. The state \( E'(\Gamma_6) \), however, occurs once only. So, its energy is a linear function of \( x \).

- The multiplets of \( \text{Ln}^{3+} \) ions with the same \( J \), e.g., the two pairs Tb\(^{3+}\), Tm\(^{3+}\) (\( J = 6 \)) and Dy\(^{3+}\), Er\(^{3+}\) (\( J = 15/2 \)), respectively, are each reduced in cubic ligand fields into the same irreducible representations.

- Exact values for LF parameters cannot be calculated reliably. However, the sign of \( B^k_q \) values can often be predicted. Consequently, the signs of \( x \) and \( W \) can be deduced, leading to the determination of the ground state.

- Systems with non-integer \( J \) have exclusively magnetic states (showing Curie paramagnetism\(^{20}\)), while in the systems with integer \( J \) ligand field ground states may be produced which are nonmagnetic, for example \( A_1(\Gamma_1) \), \( A_2(\Gamma_2) \) and \( E(\Gamma_3) \), yielding temperature independent paramagnetism (TIP).

- The \( x-(E_{LF}/W) \) diagrams are helpful not only for cubic systems but also for coordination polyhedra that don’t deviate greatly from cubic symmetry, that is, have cubic pseudo symmetry.

**Example 3.12 : Energy of the LF states of Pr\(^{3+}\) in Cs\(_2\)NaPrCl\(_6\)**

To verify Fig. 15 we use Pr\(^{3+}\) in Cs\(_2\)NaPrCl\(_6\) as an example with \( B^4_0 = 1938 \text{ cm}^{-1} \) and \( B^6_0 = 290 \text{ cm}^{-1} \) (Table 16). With the help of the entries in Table 23 as well as eqs. (102) and (103), the following data result:

\[
\begin{align*}
\frac{b_4}{b_6} &= \frac{x}{1 - |x|} = -7.665 \quad \Rightarrow \quad x = -0.8845, \quad W = \frac{b_4}{x} = 12.07
\end{align*}
\]

Table 24 exhibits the LF energies corresponding with \( x = -0.8845 \) and \( W = 12.07 \). Note that the calculated energy values, appearing in the last column of Table 24, are not identical with the observed ones (see Table 17). One reason for the discrepancy is caused by the fact that in our model only the ground multiplet \( ^3H_4 \) has been considered instead of the full basis.

The energy difference between the LF term of highest energy (\( T_2 \)) and lowest energy (\( A_1 \)) of the ground multiplet, usually called crystal field overall splitting (CFOS for short), amounts to 660 cm\(^{-1}\) (calc.) and 701 cm\(^{-1}\) (obs.).

\(^{19}\) The states are listed as a function of \( x \) in ref. [16].

\(^{20}\) Curie paramagnetism means that \( \chi_m \) increases with decreasing \( T \).
Tab. 24: Calculated energies $E_{LF}$ of the LF states of Pr$^{3+}$ in Cs$_2$NaPrCl$_6$ on the basis of spectroscopically determined values $B_0^4 = 1938$ and $B_0^6 = 290$ cm$^{-1}$ [13].

<table>
<thead>
<tr>
<th></th>
<th>$E_{LF,\text{calc.}}$/cm$^{-1}$</th>
<th>$E_{LF,\text{obs.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$(Γ$_1$)</td>
<td>$28b_4 - 80b_6$ ( W[28x - 80(1 -</td>
<td>x</td>
</tr>
<tr>
<td>T$_1$(Γ$_4$)</td>
<td>$14b_4 + 4b_6$ ( W[14x + 4(1 -</td>
<td>x</td>
</tr>
<tr>
<td>E(Γ$_3$)</td>
<td>$4b_4 + 64b_6$ ( W[4x + 64(1 -</td>
<td>x</td>
</tr>
<tr>
<td>T$_2$(Γ$_5$)</td>
<td>$-26b_4 - 20b_6$ ( W[-26x - 20(1 -</td>
<td>x</td>
</tr>
</tbody>
</table>

\( a) \) $W = 12.07$; \( x = -0.8845 \); see Example 3.12.
\( b) \) Ref. [13].
\( c) \) Crystal field overall splitting (CFOS).

Problems

7. Determine the crystal field overall splitting (CFOS) for the Dy$^{3+}$ ion in Cs$_2$NaDyCl$_6$ on the basis of Fig. 35. Apply eqs. (102) and (103) as well as the entries in Table 23 and take the $B_0^4$ and $B_0^6$ values for Dy from Table 16. (Solutions are specified in section 5.)

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3.4 Non-cubic LF

3.4.1 Ligand field operators (single electron systems)

Lowering the symmetry results in LF operators with an increasing number of terms:

- cylindrical \((D_{\infty h}, C_{\infty v})\)

  \[
  \tilde{H}_{\text{LF}}^{\text{cyl}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6
  \]  

(105)

- hexagonal \((D_{6h}, D_{3h}, D_6, C_{6v})\)

  \[
  \tilde{H}_{\text{LF}}^{\text{hex}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_0^6 \left( C_{-6}^6 + C_6^6 \right)
  \]  

(106)

- tetragonal \((D_{4h}, D_4, C_{4v}, D_{2d})\)

  \[
  \tilde{H}_{\text{LF}}^{\text{tet}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^4 \left( C_{-4}^4 + C_4^4 \right) + B_0^6 C_0^6 + B_4^6 \left( C_{-4}^6 + C_4^6 \right)
  \]  

(107)

- trigonal \((D_{3d}, D_3, C_{3v})\)

  \[
  \tilde{H}_{\text{LF}}^{\text{tri}} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^4 \left( C_{-3}^4 - C_3^4 \right) + B_0^6 C_0^6 + B_3^6 \left( C_{-3}^6 - C_3^6 \right) + B_6^6 \left( C_{-6}^6 + C_6^6 \right)
  \]  

(108)

For d electron systems only terms with \(k \leq 4\) are relevant. The number of terms for f(d) systems with cylindrical, hexagonal, tetragonal, trigonal symmetry is \(3(2), 4(2), 5(3), 6(3)\), respectively. A complete list of \(\tilde{H}_{\text{LF}}\) operators (including the symmetry \(I_h\)) is given in ref. [15].

3.4.2 4f\(^1\) system \((\text{Ce}^{3+}, \text{2F}_{5/2}; \tilde{H}_{\text{LF}}^{\text{cyl}})\)

In the following calculations the basis functions are restricted to the multiplet \(\text{2F}_{5/2}\).

Ligand field operator:

\[
\tilde{H}_{\text{LF}}^{\text{cyl}} \left( \text{2F}_{5/2} \right) = B_0^2 C_0^2 + B_0^4 C_0^4
\]  

(109)

Operator (109), acting on \(\text{2F}_{5/2}\), produces solely diagonal elements \((q = 0)\). The matrix elements \(\langle M_J | C_0^k | M_J \rangle\) for \(k = 4\) are known from matrix (83). The data for \(k = 2\) are obtained with the help of Table 8 and Table 13:

\[
\langle \pm \frac{1}{2} | C_0^2 | \pm \frac{1}{2} \rangle = \frac{8}{35}; \quad \langle \pm \frac{3}{2} | C_0^2 | \pm \frac{3}{2} \rangle = \frac{2}{35}; \quad \langle \pm \frac{5}{2} | C_0^2 | \pm \frac{5}{2} \rangle = -\frac{10}{35}.
\]

In Table 25 the results are given.

\(^{21}\) \(C_0^2 = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \); \(C_0^4_{\pm 3} = \frac{\sqrt{2}}{2} \sin^3 \theta \cos \theta e^{\pm i 3 \phi} \); \(C_0^6_{\pm 3} = \frac{\sqrt{10}}{4} \sin^3 \theta \cos \theta \left( 11 \cos^2 \theta - 3 \right) e^{\pm i 3 \phi} \); \(C_0^6_{\pm 6} = \frac{1}{\sqrt{20}} \sqrt{231} \sin \theta e^{\pm i 6 \phi} \).

\(^{22}\) \(\tilde{H}_{\text{LF}}^{\text{cyl}}\) applies also for \(D_{4d}\).

\(^{23}\) Note that under this restriction the effects of \(\tilde{H}_{\text{LF}}^{\text{cyl}}\) and \(\tilde{H}_{\text{LF}}^{\text{hex}}\) are identical.
The susceptibility equation for $\chi$ is available in the third column of Table 26. Applying Van Vleck’s equation (21) the susceptibility equation for $\chi_{\parallel}$ is

$$\chi_{\parallel} = \mu_0 N A \mu_B^2 / 3k_B T \mu_{\text{eff}}^2$$

where

$$\mu_{\text{eff}}^2 = \frac{3}{g_J^2} \left[ \frac{1}{4} \exp \left( -\frac{\Delta_1}{k_B T} \right) + \frac{9}{4} + \frac{25}{4} \exp \left( -\frac{\Delta_2}{k_B T} \right) \right] \exp \left( -\frac{\Delta_1}{k_B T} \right) + 1 + \exp \left( -\frac{\Delta_2}{k_B T} \right),$$

$$\Delta_1 = W^{(0)} - W^{(0)}_3 = \frac{8}{35} B_0^2 + \frac{5}{21} B_0^4,$$

$$\Delta_2 = W^{(0)} - W^{(0)}_5 = -\frac{12}{35} B_0^2 + \frac{4}{21} B_0^4.$$
Magnetic field perpendicular to the unique axis:
\[ \hat{H}_{\text{mag,x}} = -\gamma_e g_J \hat{J}_x B_x = -\gamma_e g_J \left( \frac{1}{2} \right) \left( \hat{J}_+ + \hat{J}_- \right) B_x \]
\[ \langle \frac{5}{2} | \hat{H}_{\text{mag,x}} | -\frac{5}{2} \rangle \]
The matrix elements \( \langle \frac{5}{2} | \hat{H}_{\text{mag,x}} | -\frac{5}{2} \rangle \) and \( \langle \frac{3}{2} | \hat{H}_{\text{mag,x}} | -\frac{3}{2} \rangle \) are zero. On account of the off-diagonal element \( \langle \pm \frac{1}{2} | \hat{H}_{\text{mag,x}} | \mp \frac{1}{2} \rangle = \frac{3}{2} g_J \mu_B B_x \), the correct zeroth-order functions have to be determined:
\[ \begin{align*}
- W_n^{(1)} & \frac{3}{2} g_J \mu_B = 0; \\
\frac{3}{2} g_J \mu_B - W_n^{(1)} & = 0; \\
W_{n(\pm)}^{(1)} & = \pm \frac{3}{2} g_J \mu_B; \\
| \psi_{\pm} \rangle & = \frac{1}{\sqrt{2}} \left( | \pm \frac{1}{2} \rangle + | -\frac{1}{2} \rangle \right).
\end{align*} \]
The \( H \) matrix reads (in units of \( g_J \mu_B B_x \)):

<table>
<thead>
<tr>
<th></th>
<th>( \frac{5}{2} )</th>
<th>( -\frac{5}{2} )</th>
<th>( \frac{3}{2} )</th>
<th>( -\frac{3}{2} )</th>
<th>( \psi_+ )</th>
<th>( \psi_- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \frac{5}{2} \rangle )</td>
<td>0</td>
<td>( \frac{\sqrt{5}}{2} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle -\frac{5}{2} \rangle )</td>
<td>0</td>
<td>0</td>
<td>( \frac{\sqrt{5}}{2} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle \frac{3}{2} \rangle )</td>
<td>( \frac{\sqrt{5}}{2} )</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>( \psi_+ )</td>
<td>( \psi_- )</td>
</tr>
<tr>
<td>( \langle -\frac{3}{2} \rangle )</td>
<td>( \frac{\sqrt{5}}{2} )</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle \psi_+ \rangle )</td>
<td>1</td>
<td>1</td>
<td>( \frac{3}{2} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle \psi_- \rangle )</td>
<td>-1</td>
<td>1</td>
<td>-( \frac{3}{2} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Table 26, column 4 and 5 the results are collected. Substituting \( W_{n}^{(0)} \), \( W_{n,x}^{(1)} \) and \( W_{n,x}^{(2)} \) in eqn. (60) yields the expression for \( \chi_{m,\pm} \):
\[ \chi_{m,\pm} = \mu_0 \frac{N_A \mu_B^2}{3 k_B T} \mu_{\text{eff,} \pm}^2 \quad \text{where} \]
\[ \mu_{\text{eff,} \pm}^2 = g_J^2 3 \left[ \left( \frac{9}{4} - \frac{4 k_B T}{\Delta_1} \right) \exp \left( -\frac{\Delta_1}{k_B T} \right) + \left( \frac{4}{\Delta_1} + \frac{5}{2 \Delta_2} \right) k_B T - \frac{5 k_B T}{2 \Delta_2} \exp \left( -\frac{\Delta_2}{k_B T} \right) \right] \]
\[ \times \left[ \exp \left( -\frac{\Delta_1}{k_B T} \right) + 1 + \exp \left( -\frac{\Delta_2}{k_B T} \right) \right]^{-1} \]
and
\[ \Delta_1 = W_{1/2}^{(0)} - W_{3/2}^{(0)} = \frac{6}{35} B_0^2 + \frac{5}{21} B_0^4 \]
\[ \Delta_2 = W_{5/2}^{(0)} - W_{3/2}^{(0)} = -\frac{12}{35} B_0^2 + \frac{4}{21} B_0^4. \]
For a polycrystalline sample the average susceptibility is
\[ \overline{\chi}_m = \frac{1}{2} \left( \chi_{m||} + 2 \chi_{m,\pm} \right) \]
This model, extended by a molecular field parameter \( \lambda_{\text{MF}} \) and a temperature-independent parameter \( \chi_0 \)
\[ (\chi_m - \chi_0)^{-1} = \overline{\chi}_m^{-1} - \lambda_{\text{MF}} \]
has been applied to the intermetallic CePt\(_5\) (CaCu\(_5\)-type: Ce\(^{3+} [4f]^1\), D\(_{6h}\)). A good adaptation to the experimental data was obtained with the parameter values \( B_0^2 = -1108 \text{ cm}^{-1} \), \( B_0^4 = -104 \text{ cm}^{-1} \), \( \lambda_{\text{MF}} = -0.43 \times 10^5 \text{ mol m}^{-3} \), and \( \chi_0 = 63 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1} \) [24, 25].
4. Isotropic spin-spin exchange couplings in dinuclear compounds

4.1 Parametrization of exchange interactions

- Heitler-London model of $H_2$

\[\begin{align*}
D_1 &= \phi_a(1)\alpha(1)\phi_b(2)\beta(2) - \phi_a(2)\alpha(2)\phi_b(1)\beta(1) \\
D_2 &= \phi_a(1)\beta(1)\phi_b(2)\alpha(2) - \phi_a(2)\beta(2)\phi_b(1)\alpha(1) \\
D_3 &= \phi_a(1)\alpha(1)\phi_b(2)\alpha(2) - \phi_a(2)\alpha(2)\phi_b(1)\alpha(1) \\
D_4 &= \phi_a(1)\beta(1)\phi_b(2)\beta(2) - \phi_a(2)\beta(2)\phi_b(1)\beta(1)
\end{align*}\]

**Construction of eigenfunctions of the total spin**

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

$D_3$ and $D_4$ are eigenfunctions $\ket{S' M_{S'}}$ of $\hat{S}'^2 = (\hat{S}_1 + \hat{S}_2)^2$ and $\hat{S}'_z = \hat{S}_{z1} + \hat{S}_{z2}$ with $S' = 1$ and $M_{S'} = 1$ and $-1$ (Spin triplet functions $\ket{11}$ and $\ket{1-1}$), respectively, while linear combinations of $D_1$ and $D_2$ yield functions with $M_{S'} = 0$: $D_1 + D_2 \implies \ket{1\ 0}$ (spin triplet function); $D_1 - D_2 \implies \ket{0\ 0}$ (spin singlet function)

\[\begin{align*}
\Phi_1 &= D_1 - D_2 \\
\Phi_2 &= D_3 \\
\Phi_3 &= D_1 + D_2 \\
\Phi_4 &= D_4
\end{align*}\]

\[\begin{align*}
\ket{0\ 0} &\quad \ket{1\ 1} &\quad \ket{1\ 0} &\quad \ket{1-1}
\end{align*}\]
\( \phi_a \) and \( \phi_b \) 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:

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

Normalised functions of the dinuclear unit:

\[
\Phi_1 = N_g \left[ \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1) \right]_{\text{sym}} \sqrt{\frac{1}{2} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]}
\]

\[
\Phi_2 \bigg| \Phi_3 \bigg| \Phi_4 = N_u \left[ \phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1) \right]_{\text{anti}} \bigg\{ \frac{\alpha(1)\alpha(2)}{\sqrt{\frac{1}{2} [\alpha(1)\beta(2) + \alpha(2)\beta(1)]}} \bigg\}_{\text{sym}}
\]

where \( N_g = (2 + 2S_{ab}^2)^{-1/2} \) and \( N_u = (2 - 2S_{ab}^2)^{-1/2} \).

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

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

\( \Rightarrow \) 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**

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

\[
E(S) = \langle \Phi_1^g \nmid \hat{H} \nmid \Phi_1^g \rangle = \frac{2(h + h_{ab}S_{ab}) + J_{ab} + K_{ab}}{1 + S_{ab}^2} \tag{117}
\]

\[
E(T) = \langle \Phi_2^g \nmid \hat{H} \nmid \Phi_2^u \rangle = \frac{2(h - h_{ab}S_{ab}) + J_{ab} - K_{ab}}{1 - S_{ab}^2} \tag{118}
\]

where
\[ h = \langle \phi_a(i) | \hat{h}(i) | \phi_a(i) \rangle \] (one-centre)

\[ h_{ab} = \langle \phi_a(i) | \hat{h}(i) | \phi_b(i) \rangle \] (transfer or hopping integral)

\[ J_{ab} = \langle \phi_a(1) \phi_b(2) | e^2/r_{12} | \phi_a(1) \phi_b(2) \rangle \] (Coulomb integral)

\[ K_{ab} = \langle \phi_a(1) \phi_b(2) | e^2/r_{12} | \phi_a(2) \phi_b(1) \rangle \] (Exchange integral).

**Example:** Evaluation of \( E(S) = \langle \Phi^g_1 | \hat{H} | \Phi^g_1 \rangle \)

1. Integration over the spin:

\[
\frac{1}{2} \langle \alpha(1) \beta(2) - \beta(1) \alpha(2) | \alpha(1) \beta(2) - \beta(1) \alpha(2) \rangle = \\
\frac{1}{2} \left[ \langle \alpha(1) \beta(2) | \alpha(1) \beta(2) \rangle - \langle \alpha(1) \beta(2) | \alpha(2) \beta(1) \rangle - \langle \alpha(2) \beta(1) | \alpha(1) \beta(2) \rangle + \langle \alpha(2) \beta(1) | \alpha(2) \beta(1) \rangle \right] = 1.
\]

2. Integration over the space:

\[ E(S) = \]

\[ N_g^2 \left[ \phi_a(1) \phi_b(2) + \phi_b(1) \phi_a(2) \right] \hat{h}(1) + \hat{h}(2) + e^2/r_{12} \left| \phi_a(1) \phi_b(2) + \phi_b(1) \phi_a(2) \right] = 2N_g^2 [2(h + h_{ab}S_{ab}) + J_{ab} + K_{ab}] .
\]

**Singlet-triplet splitting:**

\[ \Delta E(T, S) = E(T) - E(S) \approx -2K_{ab} - 4h_{ab}S_{ab} + 2S_{ab}^2 (2h + J_{ab}) \]

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

**Example:** \( L'_nCu_a - L - Cu_bL'_n \)

As distinguished from the strong covalent bond in \( H_2 \) the interactions between both magnetically active electrons is weak. \( \Rightarrow \) small \( \Delta E(T, S) \).

The highest singly occupied antibonding orbitals \( \phi_a \) and \( \phi_b \) of the fragments \( L'_nCu_a L \) and \( LCu_bL'_n \), respectively take over the role of the 1s orbitals of the H atoms. \( \phi_a \) and \( \phi_b \) have mainly d character. They are centered at the metal ions and partially delocalised in the direction of the ligands.
4.2 Heisenberg operator

The interaction between the unpaired electrons of centre 1 with the ones of centre 2 are phenomenologically described by an apparent spin-spin coupling, whose magnitude and sign are given by the spin-spin coupling parameter (exchange parameter) \( J_{\text{ex}} \):

\[
\hat{H}_{\text{ex}} = -2J_{\text{ex}} \hat{S}_1 \cdot \hat{S}_2 \quad \text{where} \quad -2J_{\text{ex}} = \Delta E(T,S)
\]  \(120\)

\( \hat{H}_{\text{ex}} \) is an effective operator, describing but not explaining the spin-spin coupling.

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

\[
-2J_{\text{ex}} \hat{S}_1 \cdot \hat{S}_2 \hat{1}\Phi_i^x = \left(\frac{3}{2}\right)J_{\text{ex}} \hat{1}\Phi_i^x,
\]

\[
-2J_{\text{ex}} \hat{S}_1 \cdot \hat{S}_2 \hat{3}\Phi_i^u = -\left(\frac{1}{2}\right)J_{\text{ex}} \hat{3}\Phi_i^u
\]

\[
\Rightarrow \Delta E(T, S) = E(T) - E(S) = -2J_{\text{ex}} \tag{121}
\]

\( J_{\text{ex}} < 0 \): singlet ground state (intramolecular antiferromagnetic interaction)

\( J_{\text{ex}} > 0 \): triplet ground state (intramolecular ferromagnetic interaction)

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

\[
\hat{S}^2 = \left(\hat{S}_1 + \hat{S}_2\right)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2
\]

\[
2\hat{S}_1 \cdot \hat{S}_2 = \hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2 = \hbar^2 \left[ S'(S' + 1) - S_1(S_1 + 1) - S_2(S_2 + 1) \right]
\]

Heisenberg operator for more than two centres:

\[
\hat{H}_{\text{ex}} = -2 \sum_{i<j} J_{\text{ex},ij} \hat{S}_i \cdot \hat{S}_j \tag{122}
\]

\[
\hat{H}_{\text{ex}} = -2J_{\text{ex}} \sum_{i<j} \hat{S}_i \cdot \hat{S}_j \tag{123}
\]

4.3 Exchange-coupled species in a magnetic field

\[
\hat{H}_{\text{ex}} = -2J_{\text{ex}} \hat{S}_1 \cdot \hat{S}_2 = -2J_{\text{ex}} \left( \hat{S}_{z1} \hat{S}_{z2} + \hat{S}_{x1} \hat{S}_{x2} + \hat{S}_{y1} \hat{S}_{y2} \right)
\]

\[
= -2J_{\text{ex}} \left[ \hat{S}_{z1} \hat{S}_{z2} + \frac{1}{2} \left( \hat{S}_{+1} \hat{S}_{-2} + \hat{S}_{-1} \hat{S}_{+2} \right) \right] \tag{124}
\]

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:

\[
\begin{array}{c|ccccc}
M_S, M_S & | \frac{1}{2} \frac{1}{2} \rangle & | -\frac{1}{2} \frac{1}{2} \rangle & | \frac{1}{2} -\frac{1}{2} \rangle & | -\frac{1}{2} -\frac{1}{2} \rangle \\
\hline
\langle \frac{1}{2} \frac{1}{2} | & -J_{\text{ex}}/2 & & & \\
\langle -\frac{1}{2} \frac{1}{2} | & J_{\text{ex}}/2 & & & \\
\langle \frac{1}{2} -\frac{1}{2} | & & -J_{\text{ex}} & & \\
\langle -\frac{1}{2} -\frac{1}{2} | & & & -J_{\text{ex}}/2 & \\
\end{array}
\]  \(125\)

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Evaluation of the diagonal element $H_{11}$:
\[-2J_{\text{ex}} \langle \frac{1}{2} \frac{1}{2} | \hat{S}_1 \hat{S}_2 | \frac{1}{2} \frac{1}{2} \rangle = -2J_{\text{ex}} \langle \frac{1}{2} \rangle \langle \frac{1}{2} \rangle = -J_{\text{ex}}/2\]

Evaluation of the off-diagonal element $H_{23}$:
\[-2J_{\text{ex}} \langle -\frac{1}{2} \frac{1}{2} | \frac{1}{2} \hat{S}_- \hat{S}_+ | -\frac{1}{2} -\frac{1}{2} \rangle = -J_{\text{ex}} \langle 1 \rangle \langle 1 \rangle = -J_{\text{ex}}\]

Results:

**Tab. 27**: Spin functions and exchange energies of the $S_1 = S_2 = \frac{1}{2}$ system

<table>
<thead>
<tr>
<th>Spin function</th>
<th>$M_{S'}$</th>
<th>$S'$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{\sqrt{2}} (</td>
<td>\frac{1}{2} -\frac{1}{2} \rangle -</td>
<td>\frac{1}{2} \frac{1}{2} \rangle)$</td>
<td>0</td>
</tr>
<tr>
<td>$</td>
<td>\frac{1}{2} \frac{1}{2} \rangle$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{\sqrt{2}} (</td>
<td>\frac{1}{2} -\frac{1}{2} \rangle +</td>
<td>\frac{1}{2} \frac{1}{2} \rangle)$</td>
<td>0</td>
</tr>
<tr>
<td>$</td>
<td>-\frac{1}{2} -\frac{1}{2} \rangle$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 18**: 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 $S' = 6$ ($E = |42J_{\text{ex}}|$) and $S' = 7$ ($E = |56J_{\text{ex}}|$) have to be added.
Magnetic susceptibility of a spin-spin-coupled system with \( S_1 = S_2 = \frac{1}{2} \)

Fig. 19: Correlation diagram of a \( S_1 = S_2 = \frac{1}{2} \) system under the influence of isotropic intramolecular spin-spin coupling \( (J_{\text{ex}} = -2 \text{ cm}^{-1}) \) and applied field

Application of the Van Vleck equation (60) to a dinuclear system with \( S_1 = S_2 = \frac{1}{2} \)
Zeeman operator:

\[
\hat{H}_{M_z} = -\gamma_e g (\hat{S}_{z1} + \hat{S}_{z2}) B_z = -\gamma_e g \hat{S}'_z B_z
\]

\[
\hat{H}'^{(1)}
\]

\[
\begin{array}{c|cccc}
S'M_S' & |11\rangle & |10\rangle & |1-1\rangle & |00\rangle \\
\hline
|11\rangle & g\mu_B B_z & & & \\
|10\rangle & & 0 & & \\
|1-1\rangle & & & -g\mu_B B_z & \\
|00\rangle & & & & 0
\end{array}
\]

Matrix elements:

\[
\langle 11|\hat{H}_{M_z}|11\rangle = g\mu_B B_z \rightarrow W_{\langle 11\rangle}^{(1)} = g\mu_B
\]

\[
\langle 1-1|\hat{H}_{M_z}|1-1\rangle = -g\mu_B B_z \rightarrow W_{\langle 1-1\rangle}^{(1)} = -g\mu_B
\]

The remaining matrix elements (Zeeman coefficients) are zero. \( W_{\langle 11\rangle}^{(1)}, W_{\langle 1-1\rangle}^{(1)}, W_{S}^{(0)} = E(S), \) and \( W_T^{(0)} = E(T) \) are substituted into the Van Vleck equation. After dividing by 2, the Bleaney-Bowers expression (\( \chi_m \) per centre) is obtained, here extended by \( \chi_0 \).

\[
\chi_m = \mu_0 N_A \mu_B^2 g^2 \left[ 1 + \frac{1}{3} \exp \left( \frac{-2J_{\text{ex}}}{k_B T} \right) \right]^{-1} + \chi_0, \quad \text{only applicable to a} \ (\text{Fig. 20}) \quad (127)
\]

61
Model calculations concerning the system \( S_1 = S_2 = \frac{1}{2} \) with positive and negative \( J_{\text{ex}} \);

\[ J_{\text{ex}} \text{ values [cm}^{-1}] :\]
- curve a: -50
- curve b: -25
- curve c: 0
- curve d: +25
- curve e: +50

Fig. 21 a: \( \chi_m-T \) diagram
Fig. 21 b: \( \chi_m^{-1}-T \) diagram
Fig. 21 c: \( \mu_{\text{eff}}-T \) diagram

Polynuclear unit of \( n \) equivalent centres:

\[
\chi_m = \frac{\mu_0}{n} \frac{N_A \mu_B^2 g^2}{3 k_B T} \sum_{S'} S'(S'+1)(2S'+1) \Omega(S') \exp \left( - \frac{E(S')}{k_B T} \right) \]

\[
\sum_{S'} (2S'+1) \Omega(S') \exp \left( - \frac{E(S')}{k_B T} \right)
\]

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 \( E(S') \):
\[
E(S') = -\frac{z J_{\text{ex}}}{n-1} [S'(S'+1) - nS(S+1)]
\]

\( z \): number of nearest neighbours of a centre
\( n \): number of interacting centres

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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. The magnetic moments are localised (no band magnetism)
  2. $S$ of the metal ions is a *good* quantum number
  3. The ground term of the metal ion has no first order orbital moment

<table>
<thead>
<tr>
<th>Examples:</th>
<th>3d⁵ high spin</th>
<th>$\rightarrow$</th>
<th>6A₁</th>
<th>3d³(O₇), 3d⁷(T₄)</th>
<th>$\rightarrow$</th>
<th>4A₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d⁶(O₇), 3d²(T₄)</td>
<td>$\rightarrow$</td>
<td>3A₂</td>
<td>3d⁹(O₇)</td>
<td>$\rightarrow$</td>
<td>2E</td>
<td></td>
</tr>
</tbody>
</table>

### 4.4 Setup of computational procedures

**Application of the computer program CONDON to**

- $4f^N-4f^N$ (homodinuclear complexes)
- $4f^N-S$ where $S = \frac{1}{2} [Cu^{2+}]$, 1, $\frac{3}{2}$ [Cr³⁺], $\frac{7}{2}$ [Gd³⁺] (heterodinuclear compl.)

\[
\hat{H} = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V(r_i) \right] + \sum_{i>j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \xi(r_i) \hat{l}_i \cdot \hat{s}_i
\]

\[
\hat{H} = \sum_{i=1}^{N} \sum_{k=0}^{\infty} \left[ B_0^{k} C_0^{k}(i) + \sum_{q=1}^{k} [B_q^{k} (C_{-q}^{k}(i) + (-1)^q C_q^{k}(i))] \right] + \sum_{i=1}^{N} \mu_B (\kappa \hat{l}_i + 2 \hat{s}_i) \cdot B_0
\]

\[
\hat{H}_{ex} = -2J_{ex} \sum_{k=1}^{N} \sum_{l=1}^{N} \hat{s}_k \cdot \hat{s}_l
\]

$B_0 = 0.001$ T (in general)

With regard to the LF symmetry of the lanthanide our choice is cubic and cylindrical for two reasons: (i) the former is isotropic and the latter anisotropic, (ii) the number of LF parameters is low [15] (cf. scheme (129)).

<table>
<thead>
<tr>
<th>point group</th>
<th>cubic</th>
<th>cylindrical</th>
<th>hexagonal</th>
<th>tetragonal</th>
<th>trigonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₇</td>
<td>Dₙ₈</td>
<td>D₉₈, D₉₉</td>
<td>D₉₄, D₉₅</td>
<td>D₉₄, D₉₅</td>
<td></td>
</tr>
<tr>
<td>T₄</td>
<td>C₂ᵥ</td>
<td>C₄ᵥ</td>
<td>C₄ᵥ, D₉₂</td>
<td>C₃ᵥ</td>
<td></td>
</tr>
<tr>
<td>no. of $B_q^{k}$’s</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>$B_q^{k}$</td>
<td>$B_4^0$ (+ $B_4^4$)</td>
<td>$B_6^2$, $B_4^4$</td>
<td>$B_0^2$, $B_4^4$</td>
<td>$B_0^2$, $B_0^6$, $B_4^4$</td>
<td>$B_0^2$, $B_0^6$, $B_3^4$, $B_6^6$</td>
</tr>
<tr>
<td>$B_0^6$ (+$B_4^4$)</td>
<td>$B_6^0$</td>
<td>$B_6^0$, $B_6^6$</td>
<td>$B_6^0$, $B_6^6$</td>
<td>$B_6^0$, $B_6^6$</td>
<td>$B_6^0$, $B_3^6$, $B_6^6$</td>
</tr>
</tbody>
</table>

\[24\) For the calculations we use only $B_0^4$ as LF parameter, except for Ce³⁺(cyl) where $B_0^2$ is considered.
Cubic ($O_h$, $T_d$)

$$\hat{H}_{\text{LF}}^{\text{cub}} = \sum_{i=1}^{N} B_0^4 \left\{ C_0^4(i) + \sqrt{5/14} \left[ C_{-4}^4(i) + C_4^4(i) \right] \right\} + B_0^6 \left\{ C_0^6(i) - \sqrt{7/2} \left[ C_{-4}^6(i) + C_4^6(i) \right] \right\}$$

fixed relations: \[ B_4^4 = \sqrt{5/14} B_0^4, \quad B_4^6 = -\sqrt{7/2} B_0^6 \]

Cylindrical ($D_{\infty h}$)

$$\hat{H}_{\text{LF}}^{\text{cyl}} = \sum_{i=1}^{N} B_0^2 C_2^2(i) + B_0^4 C_4^4(i) + B_0^6 C_6^6(i)$$

Symmetry options

<table>
<thead>
<tr>
<th>symmetry</th>
<th>cub</th>
<th>cyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_k^q$</td>
<td>$B_0^4 (+B_4^4)$</td>
<td>$B_0^2$ (Ce$^{3+}$) or $B_0^4$</td>
</tr>
<tr>
<td>coordination polyhedron</td>
<td>octahedron</td>
<td>linear</td>
</tr>
<tr>
<td>$B_k^q &gt; 0$</td>
<td>cube, tetrahedron</td>
<td>square antiprism</td>
</tr>
</tbody>
</table>

**4.5 Homodinuclear lanthanide complexes**

**4.5.1 Gd$^{3+}$–Gd$^{3+}$**

Application of eq. (128) with $S' = |S_1 - S_2|$, $|S_1 - S_2 + 1|$, \ldots $S_1 + S_2$; $S_1, S_2 = \frac{7}{2}$, $n = 2$:

$$\chi_m = \frac{\mu_0 N_A \mu_B^2 g^2}{k_B T} \left[ 1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 13e^{30x} + 15e^{42x} + 17e^{56x} \right]$$

where \[ x = J_{\text{ex}}/(k_B T) \]

$$\chi_m = \frac{\mu_0 N_A \mu_B^2 g^2}{k_B T} \left[ 1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 13e^{30x} + 15e^{42x} + 17e^{56x} \right]$$

$$J_{\text{ex}} = \pm 0.5 \text{ cm}^{-1}$$

Fig. 22: Homodinuclear complex of Gd$^{3+}$: $\mu_{\text{eff}}$ vs. $T$ plot, $J_{\text{ex}} = 0, \pm 0.5 \text{ cm}^{-1}$ ($B_0 = 0.001 \text{ T}$).
4.5.2 Group theoretical tools II

We saw in 3.3.1 that on the basis of group theory it is possible to assign the LF split terms of Ln ions. Symmetry aspects are also useful to assign the splitting produced by the combined effect of \( \hat{H}_{\text{cub}}^L \) (eq. (86)) + \( \hat{H}_{\text{ex}}^L \) (eq. (120)) on the product functions of the two interacting metal ions. The following examination is restricted to the simple case of homodinuclear Ln systems equipped with orbital contributions of the magnetic moments.

The product states split under the action of \( \hat{H}_{\text{ex}}^L \) in singlets, doublets and triplets. The split pattern is obtained in two steps:

- Application of \( \chi_{ab}(R) = \chi_a(R)\chi_b(R) \), where \( \chi_i \) is the character and \( R \) is a symmetry operation, given in the headlines of Table 28.

**Example:** The character system of the product functions \( \Gamma_{ab} \) resulting from the single-ion states \( \Gamma_a \) and \( \Gamma_b \), while \( \chi_{ab}(R) \) is the character of the (in general reducible) product state. The character of the product functions \( \chi_{\Gamma_a \otimes \Gamma_b}(R) \) is given in line 8 of Table 28.

\[
\begin{align*}
\chi_a(R) \text{ and } \chi_b(R) &= \text{characters of the irreducible representations } \Gamma_a \text{ and } \Gamma_b, \\
\chi_{ab}(R) &= \text{character of the product state.}
\end{align*}
\]

**Example:** The character system of the product functions \( \Gamma_{ab} \) resulting from the single-ion states \( \Gamma_a \) and \( \Gamma_b \), is given in line 8 of Table 28.

- Application of \( a_{\Gamma_i} = \frac{1}{h} \sum_R \chi_{\Gamma_i}^*(R)\chi_{\Gamma_i}(R) \) to determine the irreducible parts of \( \Gamma_{ab} \);

**Table 28:** Character table of the symmetry groups O and T\(_d\)

<table>
<thead>
<tr>
<th>O</th>
<th>E 8 C(_3) 3 C(_2) 6 C(_4) 6 C(_2^\prime) 6 S(_4) 6 C(_2^\prime)</th>
<th>irred. reps. of the coupled states</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(_d)</td>
<td>E 8 C(_3) 3 C(_2) 6 C(_4) 6 C(_2^\prime) 6 S(_4) 6 C(_2^\prime)</td>
<td></td>
</tr>
<tr>
<td>(\Gamma_1(\mathbb{A}_1)) (^a))</td>
<td>1 1 1 1 1 1</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_2(\mathbb{A}_2))</td>
<td>1 1 1 -1 -1 1</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_3(\mathbb{E}))</td>
<td>2 -1 2 0 0 0</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_4(\mathbb{T}_1))</td>
<td>3 0 -1 1 -1 1</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_5(\mathbb{T}_2))</td>
<td>3 0 -1 -1 1 1</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_1 \otimes \Gamma_1 ) (^b))</td>
<td>1 1 1 1 1 1</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_2 \otimes \Gamma_2 )</td>
<td>1 1 1 1 1 1</td>
<td>(\Gamma_1)</td>
</tr>
<tr>
<td>(\Gamma_3 \otimes \Gamma_3 )</td>
<td>4 1 4 0 0 0</td>
<td>(\Gamma_1 \otimes \Gamma_2 \otimes \Gamma_3)</td>
</tr>
<tr>
<td>(\Gamma_4 \otimes \Gamma_4 )</td>
<td>9 0 1 1 1</td>
<td>(\Gamma_1 \otimes \Gamma_3 \otimes \Gamma_4 \otimes \Gamma_5)</td>
</tr>
<tr>
<td>(\Gamma_5 \otimes \Gamma_5 )</td>
<td>9 0 1 1 1</td>
<td>(\Gamma_1 \otimes \Gamma_3 \otimes \Gamma_4 \otimes \Gamma_5)</td>
</tr>
<tr>
<td>(\Gamma_1 \otimes \Gamma_2 )</td>
<td>1 1 1 -1 -1 1</td>
<td>(\Gamma_2)</td>
</tr>
</tbody>
</table>

\(^a)\) Bethe (Mulliken) nomenclature.

\(^b)\) Selection of direct products for dinuclear systems with integer \( J \).

\[
\begin{align*}
\chi_{\Gamma_i}(R) &= \text{character of the } \Gamma_i \text{ for the group element } R; \\
a_{\Gamma_i} &= \frac{1}{h} \sum_R \chi_{\Gamma_i}^*(R)\chi_{\Gamma_i}(R) \text{ for the group element } R; \\
\sum_R &= \text{sum over all group elements.}
\end{align*}
\]

Result: \( \Gamma_3 \otimes \Gamma_3 \) is reducible to two singlets \((\Gamma_1, \Gamma_2)\) and a doublet \((\Gamma_3)\). The energies of the states depend on sign and size of \( J_{\text{ex}} \).
For metal ions with half-integer $J$ three types of cubic states exists: the doublets $\Gamma_6(E')$, $\Gamma_7(E'')$, and the quartet $\Gamma_8(G')$ (cf. Tab. 29).

**Tab. 29:** Character table of the double groups $O'$ and $T'_d$

<table>
<thead>
<tr>
<th>$O'$</th>
<th>$T'_d$</th>
<th>4 $C_3$</th>
<th>4 $C^2_3$</th>
<th>3 $C_2$</th>
<th>3 $C_4$</th>
<th>3 $C^4_4$</th>
<th>6 $C_2'$</th>
<th>4 $C^2_3$</th>
<th>4 $C_3$</th>
<th>3 $C_2$</th>
<th>3 $S_4$</th>
<th>3 $S^4_4$</th>
<th>6 $\sigma_d$</th>
<th>irreducible representations of the coupled states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1(A_1)^a$</td>
<td>$\Gamma_2(A_2)$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_3(E)$</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_4(T_1)$</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_5(T_2)$</td>
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<td>3</td>
<td>0</td>
<td>0</td>
<td>-1</td>
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<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_6(E')^b$</td>
<td>2</td>
<td>-2</td>
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<td>-1</td>
<td>0</td>
<td>$\sqrt{2}$</td>
<td>$-\sqrt{2}$</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$\Gamma_7(E'')$</td>
<td>2</td>
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<td>-1</td>
<td>0</td>
<td>$-\sqrt{2}$</td>
<td>$\sqrt{2}$</td>
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<td>0</td>
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<tr>
<td>$\Gamma_8(G')$</td>
<td>4</td>
<td>-4</td>
<td>-1</td>
<td>1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>$\Gamma_6 \otimes \Gamma_6$</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>$\Gamma_1 \oplus \Gamma_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_7 \otimes \Gamma_7$</td>
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<td>4</td>
<td>1</td>
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<tr>
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<td></td>
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<tr>
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<td>1</td>
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<td>-2</td>
<td>0</td>
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<td></td>
<td></td>
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<tr>
<td>$\Gamma_6 \otimes \Gamma_8$</td>
<td>8</td>
<td>8</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_7 \otimes \Gamma_8$</td>
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<td>8</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$</td>
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<td></td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>$\sqrt{2}$</td>
<td>$-\sqrt{2}$</td>
<td>0</td>
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<td>0</td>
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<td>$\sqrt{2}$</td>
<td>0</td>
<td>$\Gamma_7 \oplus \Gamma_8$</td>
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<td></td>
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<td>-2</td>
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<td>-1</td>
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<td>$\sqrt{2}$</td>
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<td></td>
</tr>
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<td>-6</td>
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<td>0</td>
<td>$-\sqrt{2}$</td>
<td>$\sqrt{2}$</td>
<td>0</td>
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<td>$\Gamma_5 \otimes \Gamma_7$</td>
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<td>0</td>
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<td>$-\sqrt{2}$</td>
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<td>$\Gamma_6 \oplus \Gamma_8$</td>
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<tr>
<td>$\Gamma_2 \otimes \Gamma_7$</td>
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<td>$-\sqrt{2}$</td>
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<tr>
<td>$\Gamma_3 \otimes \Gamma_7$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>$\Gamma_8$</td>
<td></td>
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<tr>
<td>$\Gamma_2 \otimes \Gamma_8$</td>
<td>4</td>
<td>-4</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\Gamma_8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma_3 \otimes \Gamma_8$</td>
<td>8</td>
<td>-8</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>$\Gamma_4 \otimes \Gamma_8$</td>
<td>12</td>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\Gamma_5 \otimes \Gamma_8$</td>
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<td>-12</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

$a)$ $\Gamma_1 - \Gamma_5$: integer $J$; $\Gamma_1 - \Gamma_3$: non-magnetic.

$b)$ $\Gamma_6 - \Gamma_8$: half-integer $J$; magnetic.

$c)$ Direct products where both metal ions have half-integer $J$ or $S$.

$d)$ Direct products where one metal has integer $J$ and the other has half-integer $J$ or $S$. 
4.5.3 Ce$^{3+}$–Ce$^{3+}$ (cub)

Fig. 23 exhibits the 4f$^1$ ion’s cubic LF splitting of ground and excited multiplet $^2F_{5/2}$ and $^2F_{7/2}$, respectively ($^2F_{5/2} \rightarrow \Gamma_7 + \Gamma_8$; $^2F_{7/2} \rightarrow \Gamma_7 + \Gamma_8 + \Gamma_6$). The LF ground state in octahedral coordination is the doublet $\Gamma_7$ and in tetrahedral/cubical coordination the quartet $\Gamma_8$.

Switching on $H_\text{iso}^\text{ex}$ with $J_{\text{ex}} = \pm 5 \text{ cm}^{-1}$ between the two Ce$^{3+}$ ions — each in octahedral LF — the four product states $\Gamma_7 \otimes \Gamma_7$ split into $\Gamma_1 \oplus \Gamma_4$ (see Fig. 24) with ground state $\Gamma_1$ for $J_{\text{ex}} < 0$ and $\Gamma_4$ for $J_{\text{ex}} > 0$.

The splitting of the excited 16 product functions $\Gamma_8 \otimes \Gamma_8$ by $H_\text{iso}^\text{ex}$ is more complicated (see caption of Fig. 24).

Figs. 25 and 26 display the variations $\mu_\text{eff}$ vs. $T$ for octahedral and tetrahedral/cubical LF and positive and negative $J_{\text{ex}}$. Note that $\mu_\text{eff}$ for the $\Gamma_8$ LF ground state is distinctly larger than for the doublet $\Gamma_7$ (maximum at 2.2 and 1.3, respectively, at $T = 1 \text{ K}$).

**Fig. 23:** Ce$^{3+}[4f^1]$: Cubic LF splitting of the multiplets $^2F_{5/2}$ and $^2F_{7/2}$; left: octahedral LF; right: tetrahedral/cubical LF.

**Fig. 24:** Splitting of the states of an exchange-coupled Ce–Ce unit in an octahedral LF ($B_0^4 = 1100 \text{ cm}^{-1}$); $\Gamma_7 \otimes \Gamma_7 \rightarrow \Gamma_1 \oplus \Gamma_4$: $J_{\text{ex}} > 0$, triplet ground state ($\Gamma_4$); $J_{\text{ex}} < 0$, singlet ground state ($\Gamma_1$); $\Gamma_8 \otimes \Gamma_8 \rightarrow \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus 2 \Gamma_4 \oplus 2 \Gamma_5$. 

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Fig. 25: $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Ce-Ce unit in an oct. LF ($B^0_{40} = 1100$ cm$^{-1}$); $J_{\text{ex}} > 0$, triplet ground state ($\Gamma_4$); $J_{\text{ex}} < 0$, singlet ground state ($\Gamma_1$).

Remark to Fig. 26: The product states $\Gamma_8 \otimes \Gamma_8$ are split by $H_{\text{ex}}$ into $\Gamma_1(\text{singlet (1)}) \oplus \Gamma_2(\text{singlet (1)}) \oplus \Gamma_3(\text{doublet (2)}) \oplus 2\Gamma_4(\text{triplets (3)}) \oplus 2\Gamma_5(\text{triplets (3)})$. For $J_{\text{ex}} > 0$, the sequence of split terms is given with increasing energy by (3) – (3) – (3) – (1) – (3) – (2) – (1); for $J_{\text{ex}} < 0$, this order is reversed. (Remember that only the triplets are magnetic.)

Ce$^{3+}$–Ce$^{3+}$ (cyl)

| $E_{\text{LF}}$/cm$^{-1}$ | $\left| \pm \frac{3}{2} \right>$ | $\left| \pm \frac{1}{2} \right>$ | $\left| \pm \frac{5}{2} \right>$ |
|-------------------------|----------------|----------------|----------------|
| 310                     | $^{(2)}$       | $^{(2)}$       | $^{(2)}$       |
| $\uparrow$              |                |                |                |

Scheme: Cylindrical LF splitting of the multiplet $^2F_{5/2}$ ($B^2_{00} = 600$ cm$^{-1}$; ground state: $|\pm \frac{3}{2}, \pm \frac{5}{2}\rangle$). Figure 27 exhibits that for $J_{\text{ex}} > 0$ and $T \to 0$ $\mu^\parallel_{\text{eff}} = 5.2$ while $\mu^\perp_{\text{eff}} \to 0$ (not shown in the figure), that is, strong magnetic anisotropy is observed; $\mu_{\text{eff}}^\parallel$ and $\mu_{\text{eff}}^\perp$ represent the temperature dependence of the average $\mu_{\text{eff}}$ values for positive and negative $J_{\text{ex}}$, respectively.

Fig. 26: $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Ce-Ce unit in a cubical/tet. LF ($B^4_{00} = -1100$ cm$^{-1}$); $J_{\text{ex}} > 0$, triplet ground state; $J_{\text{ex}} < 0$, singlet ground state.

Fig. 27: $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Ce–Ce unit in a cylindrical LF ($B^2_{00} = 600$ cm$^{-1}$).
4.5.4 Nd$^{3+}$–Nd$^{3+}$ (cub)

For $B_0^4 > 0$ (oct. LF; $W < 0$, $x > 0$; cf. Ex. 3.11) the LF ground state is $\Gamma_6$ while for $B_0^4 < 0$ (cub/tet) $\Gamma_8^{(2)}$ is lowest in energy (see Fig. 28).

\[ \downarrow B_0^4 < 0 \quad \text{and} \quad \downarrow B_0^4 > 0 \]

**Fig. 28:** Splitting of the Nd ground multiplet by cubic LF’s ($^4I_{9/2} \rightarrow \Gamma_6 \oplus \Gamma_8^{(1)} \oplus \Gamma_8^{(2)}$) [16].

**Fig. 29:** Splitting of the $\Gamma_8 \otimes \Gamma_8$ product states of Nd–Nd by $H_\text{ex}$ ($\rightarrow \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus 2 \Gamma_4 \oplus 2 \Gamma_5$).

**Fig. 30:** $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Nd–Nd unit in an octahedral LF (LF ground state $\Gamma_6$). For $J_\text{ex} > 0$, the ground state is magnetic (triplet $\Gamma_4$), while for $J_\text{ex} < 0$, the ground state is nonmagnetic (singlet $\Gamma_1$), that is, $\mu_{\text{eff}} \rightarrow 0$ at $T \rightarrow 0$.

**Fig. 31:** $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Nd–Nd unit in a cubical/tetrahedral LF (LF ground state $\Gamma_8$). For both situations, $J_\text{ex} < 0$ and $J_\text{ex} > 0$, the ground state is a singlet, that is, $\mu_{\text{eff}} \rightarrow 0$ as well as $\mu_{\text{eff}} \rightarrow 0$ at $T \rightarrow 0$ (cf. Fig. 29).

**Results:**

- **Fig. 30:** Only a little increase of $\mu_{\text{eff}}$ is observed after switching on $H_\text{ex}$;
- **Fig. 31:** For the ferromagnetically coupled Nd-Nd the peak of $\mu_{\text{eff}}$ at 1 K is remarkable.
4.5.5 Sm$^{3+}$–Sm$^{3+}$ (cub)

Fig. 32: $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Sm–Sm unit in oct. LF (LF ground state $\Gamma_7$). For $J_{\text{ex}} > 0$ the $\mu_{\text{eff}}$ values are only little enhanced; $\mu_{\text{eff}} \to 0$ for $J_{\text{ex}} < 0$.

Fig. 33: $\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Sm–Sm unit in cub/tet. LF (LF ground state $\Gamma_8$). Although $J_{\text{ex}} > 0$ the $\mu_{\text{eff}}$ values fall below the curve of the uncoupled system. (Obviously the magnetic contribution of the uncoupled Sm$^{3+}$ ion with LF ground state $\Gamma_8$ is larger than the contribution of the $H_{\text{ex}}$ triplet ground state of the Sm–Sm pair.)

4.5.6 Tb$^{3+}$–Tb$^{3+}$ (cub)

Taking into consideration that in the case of Tb$^{3+}$[4f$^8$] the parameter $W$ is negative for both octahedral and cubical/tetrahedral coordination polyhedra (see Table 23)\(^{a}\), the inspection of Fig. 34 shows that apart from the point of intersection of $\Gamma_2$, $\Gamma_3$ and $\Gamma_5^{(2)}$ at $E \approx 85$, $x = 0.8$, exclusively non-magnetic LF states are ground states. In consequence, the Tb$^{3+}$ ion in cubic LF is not a good candidate for the investigation of spin-spin couplings between each other.

\(^{a}\) Both Examples 3.10 and 3.11 show how to read the $x-E_{\text{LF}}/W$ diagrams.
4.5.7 Dy$^{3+}$–Dy$^{3+}$ (cub)

Fig. 35: Splitting of the Dy$^{3+}$ ground multiplet by a cubic LF ($^{3}H_{15/2} \rightarrow \Gamma_{6} \oplus \Gamma_{7} \oplus \Gamma_{8}^{(1)} \oplus \Gamma_{8}^{(2)} \oplus \Gamma_{8}^{(3)}$) [16]. The sequence of LF states for octahedral coordination is given at $x = -1$ ($B_{0}^{4} = 2000$ cm$^{-1}$, LF ground state $\Gamma_{6}$) and for cubical/tetrahedral coordination at $x = 1$ ($B_{0}^{4} = -2000$ cm$^{-1}$, LF ground state $\Gamma_{8}^{(1)}$).

Fig. 36: $\mu_{\text{eff}}$ versus $T$ plot of an exchange-coupled Dy–Dy unit in an octahedral LF ($B_{0}^{4} = 2000$ cm$^{-1}$; LF ground state $\Gamma_{6}$).

Results: For LF ground state $\Gamma_{6}$ (Fig. 36) $J_{\text{ex}} > 0$ enhances $\mu_{\text{eff}}$ in the whole temperature range while for $J_{\text{ex}} < 0$ $\mu_{\text{eff}}$ diminishes. For LF ground state $\Gamma_{8}$ (Fig. 37) it is remarkable that for $J_{\text{ex}} > 0$ $\mu_{\text{eff}}$ drops steeply from 11.3 to 2.2 far below $\mu_{\text{eff}} = 8.9$ of the uncoupled Dy-Dy pair, caused by a very weak magnet contribution of the ground triplet.
4.5.8 Dy$^{3+}$–Dy$^{3+}$ (cyl)

\[
\begin{align*}
420 & \quad (2) \quad | \pm 11/2 \rangle \\
404 & \quad (2) \quad | \pm 9/2 \rangle \\
\vdots & \quad \vdots \quad \vdots \\
315 & \quad (2) \quad | \pm 7/2 \rangle \\
305 & \quad (2) \quad | \pm 13/2 \rangle \\
\vdots & \quad \vdots \quad \vdots \\
206 & \quad (2) \quad | \pm 5/2 \rangle \\
\vdots & \quad \vdots \quad \vdots \\
114 & \quad (2) \quad | \pm 3/2 \rangle \\
\end{align*}
\]

\[ E_{\text{LF}}/\text{cm}^{-1} \]

\[
\begin{align*}
62 & \quad (2) \quad | \pm 1/2 \rangle \\
0 & \quad (2) \quad | \pm 15/2 \rangle \\
B_0^4 & = 2000 \text{ cm}^{-1}
\end{align*}
\]

\[ \uparrow \]

\[
\begin{align*}
|J\pm M_J\rangle : |15/2\pm 15/2\rangle
\end{align*}
\]

Fig. 38: Exchange-coupled dinuclear Dy unit in cylindrical LF ($B_0^4 = 2000 \text{ cm}^{-1}$; LF ground state $|J \pm M_J\rangle$: $|15/2 \pm 15/2\rangle$).

\begin{tabular}{|c|c|c|c|}
\hline
$J_{\text{ex}}/\text{cm}^{-1}$ & $\mu_{\text{eff}}^\parallel$ & $\mu_{\text{eff}}^\perp$ & \\
\hline
Dy–Dy(cyl) & $+$1 & & \\
Dy(cyl)–Cr & $+$5 & & \\
Tb(cyl)–Cr & $+$5 & & \\
\hline
\end{tabular}

4.5.9 Ln–Ln pair: Temporary résumé of $\mu_{\text{eff}}$ for $J_{\text{ex}} > 0$ (rating $+/–$)

\begin{tabular}{|c|c|c|c|c|c|}
\hline
$\text{Ln}^{3+}$ & $\text{Ce}^{3+}$ & $\text{Nd}^{3+}$ & $\text{Sm}^{3+}$ & $\text{Tb}^{3+}$ & $\text{Dy}^{3+}$ \\
\hline
\text{free ion} & 2.54 & 3.62 & 0.84 & 9.72 & 10.64 \\
\text{cub} & $–$ & $+/–$ & $–$ & $–$ & $+$ \\
\text{cyl} & $++$ & 2.3 & 3.8 & 0.48 & TIP & 11.2 \\
\hline
\end{tabular}

1. Cubic Ln systems are no good candidates for large $\mu_{\text{eff}}$;
2. Particularly Sm and Tb are unsuitable in cubic LF;
3. Dy in cylindrical LF is an excellent candidate.

\[ a) \text{ At } T = 2 \text{K.} \quad b) \text{Examination is still pending.} \]
4.6 Heterodinuclear transition metal–lanthanide systems

4.6.1 \( p^2P_{1/2} - s^2S_{1/2} \) molecule

As an introduction, the spin-spin-coupling \( H_{ex} \) within a \( p^1-s^1 \) unit is considered, where the six states of \( p^1 \) are split by \( H_{SO} \) into the quartet \( 2^2P_{1/2} \) and the doublet \( 2^2P_{1/2} \). We assume \( H_{SO} \gg H_{ex} \) and restrict the calculations to \( 2^2P_{1/2}-2^2S_{1/2} \). The corresponding basis functions \( |JM_J \rangle = |1/2 \pm 1/2 \rangle \) of the multiplet \( 2^2P_{1/2} \) are given in Table 30\(^{25}\).

Table 30: \( 2^2P_{1/2} \) functions \( |JM_J \rangle = |1/2 \pm 1/2 \rangle \) of the spin-orbit coupled \( p^1 \) system

| \( \psi \) | \( |ML MS \rangle \) | \( |JM_J \rangle \) | \( M_J = ML + MS \) | \( J \) |
|---|---|---|---|
| \( \psi_3 \) | \( -\sqrt{\frac{2}{3}} |1 - \frac{1}{2}\rangle + \sqrt{\frac{1}{3}} |0 \frac{1}{2}\rangle \) | \( |\frac{1}{2} \frac{1}{2}\rangle \) | \( \frac{1}{2} \) | \( \frac{1}{2} \) |
| \( \psi_5 \) | \( \sqrt{\frac{2}{3}} |1 \frac{1}{2}\rangle - \sqrt{\frac{1}{3}} |0 \frac{1}{2}\rangle \) | \( |\frac{1}{2} - \frac{1}{2}\rangle \) | \( -\frac{1}{2} \) |

Since the calculations are restricted to the ground multiplet \( J = 1/2 \), \( \hat{H}_{ex} \) can be applied in the form

\[
\hat{H}_{ex} = -2J_{ex} (g_{J} - 1) \mathbf{S} \cdot \mathbf{S} = -2(g_{J} - 1)J_{ex} \left( \hat{J}_z \hat{S}_z + \hat{J}_x \hat{S}_x + \hat{J}_y \hat{S}_y \right)
\]

De Gennes

\[
= -2(g_{J} - 1)J_{ex} \left( \hat{J}_z \hat{S}_z + \frac{1}{2} \left( \hat{J}_+ \hat{S}_+ + \hat{J}_- \hat{S}_- \right) \right)
\]

with the advantage, that for the \( p \) system the basis functions \( |JM_J \rangle \) can be used.

Basis functions of \( p-s \): \( |ML MS \rangle \), \( M_J \) referring to the \( p \) electron and \( MS \) to the \( s \) electron

According to \( g_{1/2} = \frac{2}{3} \) for \( 2^2P_{1/2} \) (see eq. (2)), the De Gennes factor is \( g_{1/2} - 1 = -\frac{1}{3} \), and \( (g_{J} - 1)J \) is the component \( S_J \) of \( S \) in direction of \( J \).

\[\text{H-Matrix of operator (131)}: \]

| \( M_J MS \) | \( \frac{1}{2} \frac{1}{2} \) | \( -\frac{1}{2} \frac{1}{2} \) | \( \frac{1}{2} -\frac{1}{2} \) | \( -\frac{1}{2} -\frac{1}{2} \) |
|---|---|---|---|
| \( \langle \frac{1}{2} \frac{1}{2} \rangle \) | \( \frac{1}{6} J_{ex} \) | | |
| \( \langle -\frac{1}{2} \frac{1}{2} \rangle \) | | \( -\frac{1}{6} J_{ex} \) \( \frac{1}{3} J_{ex} \) |
| \( \langle \frac{1}{2} -\frac{1}{2} \rangle \) | | | \( \frac{1}{3} J_{ex} \) \( -\frac{1}{6} J_{ex} \) |
| \( \langle -\frac{1}{2} -\frac{1}{2} \rangle \) | | | | \( \frac{1}{6} J_{ex} \) |

(132)

Evaluation of the diagonal element \( H_{11} \):

\[-2\left( -\frac{2}{3} \right) J_{ex} \langle \frac{1}{2} \frac{1}{2} | \hat{J}_z \hat{S}_z | \frac{1}{2} \frac{1}{2} \rangle = \left( \frac{3}{2} \right) J_{ex} \langle \frac{1}{2} \left( \frac{1}{2} \right) \rangle = \frac{1}{6} J_{ex} \]

\(^{25}\) The complete set of basis functions of \( 2^2P_{1/2} \) and \( 2^2P_{3/2} \) is given Table 6.
Evaluation of the off-diagonal element $H_{23}$:

$$\left(\frac{2}{3}\right) J_{ex} \langle -\frac{1}{2} \mid \left(\frac{1}{2}\right) \hat{J}_- \hat{S}_+ \mid \frac{1}{2} - \frac{1}{2} \rangle = \left(\frac{2}{3}\right) J_{ex} \langle \frac{1}{2} \rangle_1 \langle 1 \rangle_1 = \frac{1}{3} J_{ex}$$

**Result:** Compared to the singlet-triplet splitting of an exchange-coupled $s^1-s^1$ molecule, the situation is inverted for a $p^1-s^1$ molecule if strong spin-orbit coupling within the $p^1$ system is taken into consideration: In the case of antiferromagnetic exchange coupling ($J_{ex} < 0$), the triplet state is lowest in energy.
4.6.2 \( \text{Gd}^{3+} - \text{Cu}^{2+} (S = 1/2) \)

\[ 4.6.2 \quad \text{Gd}^{3+} - \text{Cu}^{2+} (S = 1/2) \]

Fig. 39: \( \mu_{\text{eff}} \) vs. \( T \) plot of a ferromagnetically coupled and an uncoupled \( \text{Gd}^{3+} - \text{Cu}^{2+} \) unit as a function of the applied field: \( J_{\text{ex}} = 5 \text{ cm}^{-1} \) (solid lines), \( J_{\text{ex}} = 0 \) (dotted lines); \( g_{\text{Gd}} = g_{\text{Cu}} = 2; B_0 = 0.01 \) (a), 0.1 (b), 1.0 T (c).

The solid lines in Fig. 39 refer to a heterodinuclear \( \text{Gd}^{3+} - \text{Cu}^{2+} \) complex (\( S_{\text{Gd}} = 7/2; S_{\text{Cu}} = 1/2 \)) of ferromagnetically coupled spins with the exchange parameter \( J_{\text{ex}} = 5 \text{ cm}^{-1} \). Solely for \( B_0 = 0.01 \text{ T} \) (a) the expected plateau at \( \mu_{\text{eff}} = 8.94 \) is obtained at \( T \leq 2 \text{ K} \) except for \( T \leq 0.2 \text{ K} \). In order to adjust \( J_{\text{ex}} \) by fitting procedures to corresponding experimental data, it is justified to apply a susceptibility equation valid for \( B_0 \rightarrow 0 \) (Van Vleck approach). For measurements with the stronger field 0.1 T (b) and all the more 1 T (c) deviations are obvious, which are not adequately described by the simple model. They could be misinterpreted, however, as an additional antiferromagnetic intermolecular spin-spin coupling. A similar problem arises if a corresponding uncoupled system is considered (Fig. 39, dotted lines). A straight line parallel to the \( T \) axis is obtained at \( \mu_{\text{eff}} = 8.13 \) for \( B_0 \rightarrow 0 \) (curve a) while increasing deviations from this reference line to lower values are again obvious with increasing field (b, c), falsely interpreted as an intramolecular spin-spin coupling of antiferromagnetic nature. Hence, either the measurements are carried out at very weak applied fields or the extended susceptibility formula is used as in the given model calculations.
4.6.3 \( \text{Ce}^{3+}\) (cub)–Cu\(^{2+}\) (\( S = 1/2 \))

After discussion of the \( p^1−s^1 \) case under the influence of \( H_{SO} + H_{ex} \), we pass to the \( f^1−s^1 \) system perturbed by \( H^\text{SO} + H^\text{LF} + H_{ex} \). To clarify the computational procedures, the low-temperature magnetic behaviour of a system consisting of a \( 4f^1 \) ion, exchange-coupled to a pure spin system with \( S = \frac{1}{2} \), is described with restricted basis functions. After switching on \( H^\text{SO} \) and \( H^\text{LF} \) acting on the \( \text{Ce}^{3+} \) ion, only the ground doublet \( \Gamma_7 \) (\( E'' \)) is considered for spin-spin coupling with the \( ^2S_{1/2} \) system (represented here by Cu\(^{2+}\) [3d\(^9\)]).

The procedure is outlined by three steps:

\[
\begin{aligned}
4f^1 &\xrightarrow{H_{SO}} 2F_{5/2} + 2F_{7/2} \\
2F_{5/2} &\xrightarrow{H^\text{LF}} \Gamma_7 + \Gamma_8 \\
\Gamma_7 \otimes \Gamma_6 &\xrightarrow{H_{ex}} \Gamma_2 + \Gamma_5
\end{aligned}
\]

The wave functions of the \( \text{Ce}^{3+} \) doublet \( \Gamma_7 \) are given in Tab. 32. The state is assumed to be thermally isolated (similar to \( ^2P_{1/2} \) of the \( p−s \) molecule (see section 4.6.1) on account of \( H_{SO} > H^\text{LF}(\text{oct}) \gg H_{ex} \)) and exchange-coupled to the \( S = \frac{1}{2} \) pure spin system.

**Table 32:** Doublet wavefunctions of \( 2F_{5/2} \) perturbed by a cubic ligand field

| \( |\tilde{M}\rangle \) | \( |M_J\rangle \) |
|---|---|
| \( E''\alpha'' \) | \( \sqrt{\frac{1}{6}} |\frac{5}{2}\rangle - \sqrt{\frac{1}{6}} |\frac{3}{2}\rangle \) | \( \Gamma_7 \) |
| \( E''\beta'' \) | \( \sqrt{\frac{1}{6}} |\frac{5}{2}\rangle - \sqrt{\frac{1}{6}} |\frac{3}{2}\rangle \) |

Application of \( \hat{H}_{ex} \) (eq. (131)) with \( g_J = \frac{6}{7} \) produces the \( 4 \times 4 \) matrix given in scheme (133) which is similar to scheme (132), apart from the signs of the matrix elements:

(133)

<table>
<thead>
<tr>
<th>( M_J M_S )</th>
<th>( E''\alpha'', \frac{1}{2} )</th>
<th>( E''\beta'', \frac{1}{2} )</th>
<th>( E''\alpha'', -\frac{1}{2} )</th>
<th>( E''\beta'', -\frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle E''\alpha'', \frac{1}{2} \rangle )</td>
<td>( -\frac{5}{42} J_{ex} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle E''\beta'', \frac{1}{2} \rangle )</td>
<td>( \frac{5}{42} J_{ex} )</td>
<td>( -\frac{5}{21} J_{ex} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle E''\alpha'', -\frac{1}{2} \rangle )</td>
<td>( -\frac{5}{21} J_{ex} )</td>
<td>( \frac{5}{42} J_{ex} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle E''\beta'', -\frac{1}{2} \rangle )</td>
<td>( -\frac{5}{42} J_{ex} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Evaluation of the diagonal element \( H_{11} \) (De Gennes factor: \( g_J − 1 = \frac{6}{7} − 1 = −\frac{1}{7} \)):

\[
-2(-\frac{1}{7}) J_{ex} \langle E''\alpha'', \frac{1}{2} | \hat{J}_z \hat{S}_z | E''\alpha'', \frac{1}{2} \rangle = \left( \frac{5}{7} \right) \left[ \left( \frac{5}{6} \right) \left( \frac{1}{2} \right) + \left( \frac{5}{6} \right) \left( -\frac{3}{2} \right) \left( \frac{1}{2} \right) \right] J_{ex} = -\frac{5}{42} J_{ex}
\]

**Results:**

\[
\begin{align*}
E_{\text{singlet}} &= \frac{15}{42} J_{ex} \\
E_{\text{triplet}} &= -\frac{5}{42} J_{ex} \\
\Delta E &= E_{\text{triplet}} - E_{\text{singlet}} = -\frac{10}{21} J_{ex}
\end{align*}
\]

Simulation calculations: For \( J_{ex} > 0 \), the triplet state \( \Gamma_5 \) is the ground state while for \( J_{ex} < 0 \) the singlet \( \Gamma_2 \) has the lowest energy (as is predicted for the restricted basis).
Figs. 40 and 41 exhibit the corresponding $\mu_{\text{eff}}$ vs. $T$ plots and Figs. 42 and 43 the $\chi_m^{-1}$ vs. $T$ plots\textsuperscript{26}. Inspecting Fig. 40 it is remarkable that at $T > 5$ K the antiferromagnetic spin-spin coupling yields higher $\mu_{\text{eff}}$ values than the ferromagnetic spin-spin coupling. This finding is the consequence of the fact that corresponding to Hund’s third rule $J$ is $L - S$ and that for a spin-spin coupling of antiferromagnetic nature the spin parts of the $J$–$S$ dinuclear unit cancel to a certain degree, so that the orbital part is enhanced. As opposed to that, the spin-spin coupling of ferromagnetic nature leads to a further weakening of the orbital part of the 4f$^1$ configuration. The fact that the $\mu_{\text{eff}}$ values of the uncoupled Ce–Cu unit at $T < 2$ K are larger than the $\mu_{\text{eff}}$ values of both coupled systems is the consequence of the reduction of orbital parts according to the exchange splitting.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig40.png}
\caption{$\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Ce$^{3+}$–Cu$^{2+}$ ($S = \frac{1}{2}$) unit; Ce in octahedral LF ($B_0^4 = 1 100$ cm$^{-1}$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig41.png}
\caption{$\mu_{\text{eff}}$ vs. $T$ plot of an exchange-coupled Ce$^{3+}$–Cu$^{2+}$ ($S = \frac{1}{2}$) unit at $T < 1.5$ K; Ce in octahedral LF ($B_0^4 = 1 100$ cm$^{-1}$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig42.png}
\caption{$\chi_m^{-1}$ vs. $T$ plot of the exchange-coupled Ce$^{3+}$ (oct)–Cu$^{2+}$ ($S = \frac{1}{2}$) unit.}
\end{figure}

Notice that, apart from the lowest temperatures, the spin-spin coupling produces small parallel shifts of the $\chi_m^{-1}$–$T$ curve of the uncoupled system (Fig. 42, black line). The shifts are described by 
\[(\chi_m^{-1})' = \chi_m^{-1} - \lambda_{\text{MF}}\]
where $(\chi_m^{-1})'$ corresponds with the shifted curve and $\lambda_{\text{MF}}$ is the molecular field parameter.

\textsuperscript{26} The data presented in Figs. 40 – 43 have been calculated with the full basis set of $14 \times 2 = 28$ functions (using the computer program CONDON).
Fig. 43 displays that at $T < 5\text{K}$ the blue curve ($J_{\text{ex}} < 0$) tends to temperature independent paramagnetism (TIP), whereas the red curve ($J_{\text{ex}} > 0$) exhibits Curie paramagnetism.

In Fig. 43 the black reference curve of the uncoupled system follows Curie’s law in a good approximation on account of the thermally isolated states $\Gamma_7(\text{Ce})$ and $\Gamma_6(\text{Cu})$. Both states show linear $\chi_m^{-1}T$ behaviour (apart from a very small 2nd order Zeeman contribution of $\Gamma_7$).

4.6.4 Nd$^{3+}$(cub)–Cu$^{2+}(S = 1/2)$ and Nd$^{3+}$(cub)–Cr$^{3+}(S = 3/2)$

Figs. 44 and 45 exhibit the $\mu_{\text{eff}}$ vs. $T$ plots of the heterodinuclear species Nd–$(S = 1/2)$ (Cu$^{2+}$) and Nd–$(S = 3/2)$ (Cr$^{3+}$), respectively, in cubic LF. Inspecting both Figures it is remarkable that, similar to the Ce-Cu system (Figs. 40 – 43) the antiferromagnetic spin-spin coupling leads to higher $\mu_{\text{eff}}$ values than the ferromagnetic coupling on account
of the fact that the residual component of the spin-spin coupling strengthens the orbital part of the lanthanide’s moment.

Fig. 44: \( \mu_{\text{eff}} \) vs. \( T \) diagram of an exchange-coupled Nd\(^{3+}\)–Cu\(^{2+}\) unit with Nd in a cubic LF (\( B_0^4 = 2000 \text{ cm}^{-1} \)) and Cu regarded as a pure spin system \( S = \frac{1}{2} \).

4.6.5 Dy\(^{3+}\)(cub)–Cu\(^{2+}\)(\( S = \frac{1}{2} \)), Dy\(^{3+}\)(cyl)–Cr\(^{3+}\)(\( S = \frac{3}{2} \)), Tb\(^{3+}\)(cyl)–Cr\(^{3+}\)(\( S = \frac{3}{2} \))

Fig. 45: \( \mu_{\text{eff}} \) vs. \( T \) diagram of an exchange-coupled Nd\(^{3+}\)–Cr\(^{3+}\) unit with Nd in a cubic LF (\( B_0^4 = 2000 \text{ cm}^{-1} \)) and Cr regarded as a pure spin system \( S = \frac{3}{2} \).

Fig. 46: \( \mu_{\text{eff}} \) vs. \( T \) diagram of an exchange-coupled Dy\(^{3+}\)–Cu\(^{2+}\) unit where Dy is in a cubic LF (\( B_0^4 = 2000 \text{ cm}^{-1} \)) whereas Cu is regarded as a pure spin system \( S = \frac{1}{2} \).

Fig. 47: Dy–Dy(cyl): \( \parallel \mu_{\text{eff}} \), Dy–Cr: \( \mu_{\text{eff}} \), Tb–Cr: \( \mu_{\text{eff}} \)
4.6.6 Gd$^{3+}$–V$^{3+}$

The 4f ion (Gd$^{3+}$, $^8S_{7/2}$) is regarded as a pure spin system, unaffected by ligands, zero-field splitting ignored. The electronic situation of the transition metal ion (for example V$^{3+}$) depends on $H_{LF}$ and $H_{SO}$, demonstrated in Figure 48.

![Diagram showing $\mu_{eff}$ versus $T$ and $\chi^{-1}$ versus $T$](image)

**Fig. 48:** $\mu_{eff}$ versus $T$ and $\chi^{-1}$ versus $T$ diagrams showing the predicted magnetic behaviour of V$^{3+}$[3d$^2$] ion in octahedral (solid lines) and orthorhombic surrounding (dashed lines); parameter values [6]: Racah parameters $B = 861 \text{ cm}^{-1}$, $C = 4165 \text{ cm}^{-1}$, $\zeta = 209 \text{ cm}^{-1}$, $B_0^4 = 25000 \text{ cm}^{-1}$ for the octahedral coordination, $B_0^2 = -34000$, $B_2^2 = -16000$, $B_0^4 = 3500$, $B_2^4 = 1800$, $B_4^4 = 2300 \text{ cm}^{-1}$ for orthorhombic symmetry.

While the octahedral system shows between 100 K and 300 K nearly temperature independent paramagnetism, the orthorhombic one approximates to a Curie paramagnet with only slightly varying $\mu_{eff}$. The two situations differ distinctly in the orbital contributions to the magnetic moment. The expected magnetic properties of the V$^{3+}$–Gd$^{3+}$ unit is given in Figures 49 and 50).

If V$^{3+}$ is octahedrally coordinated, $\mu_{eff}$ in the uncoupled situation ($J_{ex} = 0$) is temperature dependent owing to the loss of magnetic activity of vanadium with decreasing temperature (see the solid reference line in Figure 49, $\mu_{eff} = 8.37 \text{ (300 K)} \rightarrow 8.05 \text{ (50 K)}$). When $T$ approaches zero solely the magnetism of Gd$^{3+}$ contributes. The uncoupled system with vanadium in orthorhombic symmetry, however, exhibits a temperature independent $\mu_{eff}$, except for $T \leq 25 \text{ K}$. This is the consequence of the nearly total quenching of orbital contributions of vanadium’s valence electrons owing to the low-symmetric ligand field. In consequence, the transition metal ion behaves in a wide temperature range as a pure spin system $S = 1$. 

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Fig. 49: $\mu_{\text{eff}}$ versus $T$ diagram ($B_0 = 0$) showing the predicted magnetic behaviour of an exchange-coupled 3d$^2$ (oct)–4f$^7$ species where $J_{\text{ex}} = 0, \pm 2, \pm 5, \pm 10 \text{ cm}^{-1}$; insert: model calculations for $J_{\text{ex}} = 2 \text{ cm}^{-1}$ and $B_0 = 0, 1, \text{ and } 5 \text{ T}$.

Fig. 50: $\mu_{\text{eff}}$ versus $T$ diagram ($B_0 = 0$) showing the predicted magnetic behaviour of an exchange-coupled 3d$^2$ (rhomb)–4f$^7$ species where $J_{\text{ex}} = 0, \pm 2, \pm 5, \pm 10 \text{ cm}^{-1}$; insert: model calculations for $J_{\text{ex}} = 2 \text{ cm}^{-1}$ and $B_0 = 0, 1, \text{ and } 5 \text{ T}$.
Switching on the intramolecular spin-spin coupling $J_{\text{ex}}$ we see a distinct dependence of the magnetic properties on the sign of $J_{\text{ex}}$ and the transition metal’s symmetry: Regarding first the cubic case with a ferromagnetic coupling ($J_{\text{ex}} > 0$), $\mu_{\text{eff}}$ increases, for antiferromagnetic coupling ($J_{\text{ex}} < 0$) $\mu_{\text{eff}}$ decreases compared to the reference line. However, in contrast to pure spin systems, where we expect a plateau at low temperature, the course is more complicated reflecting the reduction of vanadium’s paramagnetism. If the transition metal site has only orthorhombic symmetry significant alterations are ascertained in the course of $\mu_{\text{eff}}$ versus $T$: At low temperature plateaus become apparent at $\mu_{\text{eff}} \approx 9.9$ and $5.9$ for positive and negative $J_{\text{ex}}$ corresponding to systems with total spin $S = 9/2$ and $5/2$, respectively. The decrease of $\mu_{\text{eff}}$ at the lowest temperatures is again due to small orbital contributions of vanadium’s electronic system.

Problems

9. The Bleaney-Bowers formula, eq. (127), approaches for high temperature the Curie-Weiss law $\chi_m = C/(T - \theta)$. Determine the relation between $J_{\text{ex}}$ and $\theta$. Is the result in agreement with the relation $\theta = (2S(S + 1)/3k_B) \sum_i z_i J_{\text{ex}}$?

10. What magnetic behaviour is obtained, if in the Bleaney-Bowers formula, eq. (127), $J_{\text{ex}}$ is set to 0?

11. What are the electronic ($4f^N$) and the LF symmetry relevant preconditions for building up a homodinuclear Ln molecule with large $\mu_{\text{eff}}$ and high magnetic anisotropy?

12. Magnetochemical results are often presented as $\chi_m - T$, $\chi_m^{-1} - T$ or $\mu_{\text{eff}} - T$ diagrams. What type of diagram is suited for (a) Curie paramagnetism, (b) intramolecular ferromagnetic interactions, (c) intramolecular antiferromagnetic interactions, (d) diamagnetic behaviour, (e) TUP behaviour?

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

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

15. 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?

16. For a polynuclear complex one observes at high temperature Curie-Weiss behaviour with $\theta > 0$ and in the low-temperature region field-dependent susceptibilities. What magnetic collective effect can be expected?

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

18. You notice that the paramagnetic properties of a homodinuclear molecular compound is not satisfactorily described with the corresponding eq. (128). What simple extensions of the model are in principle possible?
5 Solutions

1. Verify the Russell-Saunders ground multiplets for Nd\(^{2+}\) and Er\(^{3+}\) given in Table 2.

\[\text{Nd}^{2+}[4f^4]: L = 6, S = 2, J = 4 \implies ^5I_4.\]

\[\text{Er}^{3+}[4f^{11}]: L = 6, S = 3/2, J = 15/2 \implies ^5I_{15/2}.\]

2. Evaluate the susceptibility equation for a free \(p^1\) system perturbed by spin-orbit coupling. (Hint: Apply eq. (3); note that for the single-electron system \(\zeta_{LS} \equiv \zeta\).)

\[\begin{align*}
g_{1/2} & = 1 + \left(\frac{5}{3}\right) + \left(\frac{2}{3}\right) - 2 \left(\frac{1}{2}\right) = \frac{2}{3} \\
g_{3/2} & = 1 + \left(\frac{5}{3}\right) + \left(\frac{2}{3}\right) + 2 \left(\frac{1}{2}\right) = \frac{4}{3} \\
\Lambda_{1/2} & = \left(\frac{5}{3}\right)^2 \left(\frac{2}{3}\right) + 2 \left(\frac{2}{3} - 1\right) \left(\frac{2}{3} - 2\right) k_B T \frac{1}{\zeta} = \frac{1}{3} + \frac{8 k_B T}{9 \zeta} \\
\Lambda_{3/2} & = \left(\frac{5}{3}\right) \left(\frac{3}{2}\right) \left(\frac{2}{3}\right) + 2 \left(\frac{2}{3} - 1\right) \left(\frac{4}{3} - 2\right) k_B T \frac{1}{\zeta} = \frac{20}{3} - \frac{4 k_B T}{9 \zeta}
\end{align*}\]

\[\chi_m = \mu_0 \frac{N_A \mu_B^2}{3 k_B T} \times \frac{Z}{N}, \quad \text{where}
\]

\[\begin{align*}
Z & = 2 \left(\frac{5}{3} + \frac{8 k_B T}{9 \zeta}\right) \exp \left(-\frac{3 \zeta}{8 k_B T}\right) + 4 \left(\frac{20}{3} - \frac{4 k_B T}{9 \zeta}\right) \exp \left(-\frac{15 \zeta}{8 k_B T}\right) \\
N & = 2 \exp \left(-\frac{3 \zeta}{8 k_B T}\right) + 4 \exp \left(-\frac{15 \zeta}{8 k_B T}\right)
\end{align*}\]

\[\chi_m = \mu_0 \frac{N_A \mu_B^2}{3 k_B T} \left[\frac{1}{3} + \frac{8 k_B T}{9 \zeta} + \left(\frac{40}{3} - \frac{8 k_B T}{9 \zeta}\right) \exp \left(-\frac{3 \zeta}{2 k_B T}\right)\right] \quad \text{(134)}
\]

To verify eq. (134), it is recommended to develop the susceptibility equation for the borderline case \(\zeta \to 0\) (use the approximation \(\exp \pm x \approx 1 \pm x\)). For an uncoupled system the relation \(\mu = \sqrt{L(L + 1) + 4S(S + 1)} \mu_B\) holds, so that for the \(p^1\) system \((L = 1, S = 1/2)\) the permanent magnetic moment \(\mu = \sqrt{5} \mu_B\) and the susceptibility equation \(\chi_m = \mu_0 5 N_A \mu_B^2 / (3k_B T)\) must be the results.

3. Use the spherical harmonics in Table 3 and construct the real functions \(d_{x^2-y^2}\) and \(d_{xy}\) with the help of eqs. (8). Verify the results with the data given in Table 4.

\[\begin{align*}
\frac{1}{\sqrt{2}} [\psi_{n,l,m_l} + \psi_{n,l,-m_l}] & = \frac{1}{\sqrt{2}} \left[\sqrt{\frac{15}{32 \pi}} \sin^2 \theta \left(\cos 2\phi + i \sin 2\phi + \cos 2\phi - i \sin 2\phi\right)\right] \\
& = \sqrt{\frac{15}{16 \pi}} \sin^2 \theta \cos 2\phi = d_{x^2-y^2} \\
\frac{1}{\sqrt{2}} [\psi_{n,l,m_l} - \psi_{n,l,-m_l}] & = \frac{1}{\sqrt{2}} \left[\sqrt{\frac{15}{32 \pi}} \sin^2 \theta \left(\cos 2\phi + i \sin 2\phi - \cos 2\phi + i \sin 2\phi\right)\right] \\
& = \sqrt{\frac{15}{16 \pi}} \sin^2 \theta \sin 2\phi = d_{xy}
\end{align*}\]
4. Calculate the matrix elements \( \langle l, m_l \mid \hat{q} \mid l, m_l' \rangle \) (where \( q \) stands for \( z, +, - \)):

(a) \( \langle 0,0 \mid \hat{\ell}_z \mid 0,0 \rangle = 0 \)

(b) \( \langle 2,2 \mid \hat{\ell}_+ \mid 2,1 \rangle = \sqrt{2} \cdot 3 - 1 \cdot 2 \ h \langle 2,2 \mid 2,2 \rangle = 2 \ h \\
\)

(c) \( \langle 2,2 \mid \hat{\ell}_+^2 \mid 2,0 \rangle = \sqrt{6} \ h \langle 2,2 \mid 2,1 \rangle = 2 \sqrt{6} \ h^2 \langle 2,2 \mid 2,2 \rangle = 2 \sqrt{6} \ h^2 \\
\)

(d) \( \langle 2,0 \mid \hat{\ell}_+ \hat{\ell}_- \mid 2,0 \rangle = \sqrt{6} \ h \langle 2,0 \mid 2,0 \rangle \langle 2,0 \mid 2,1 \rangle = 6 \ h^2 \\
\)

5. The 14 microstates \( |m_l m_s \rangle \) of an \( f^1 \) system \( (l = 3, \ s = \frac{1}{2}) \) yield under the influence of spin-orbit coupling 14 eigenstates \( |j m_j \rangle \) which, apart from the states \( |\frac{5}{2} \pm \frac{1}{2} \rangle \) are linear combinations of two microstates each. Use Table 7 to evaluate the vector coupling coefficients for the coupled states \( |\frac{5}{2} \pm \frac{3}{2} \rangle, |\frac{5}{2} \pm \frac{1}{2} \rangle, |\frac{1}{2} \pm \frac{3}{2} \rangle, \) and \( |\frac{1}{2} \pm \frac{1}{2} \rangle \). Control your results with the entries of Table 8.

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?

(a) \( ^1S: J = 0 \) (1 state)

(b) \( ^2P: J = \frac{1}{2} \) (2), \( J = \frac{3}{2} \) (4)

(c) \( ^3P: J = 0 \) (1), \( J = 1 \) (3), \( J = 2 \) (5)

(d) \( ^3D: J = 1 \) (3), \( J = 2 \) (5), \( J = 3 \) (7)

(e) \( ^4D: J = \frac{1}{2} \) (2), \( J = \frac{3}{2} \) (4), \( J = \frac{5}{2} \) (6), \( J = \frac{7}{2} \) (8)

7. Determine the crystal field overall splitting (CFOS) for the Dy\(^{3+} \) ion in Cs\(_2\)NaDyCl\(_6\) on the basis of Fig. 35. Apply eqs. (102) and (103) as well as the entries in Table 23 and take the \( B_{0}^0 \) and \( B_{0}^0 \) values for Dy from Table 16.

\[
\beta_J \tilde{F}(4) B_{0}^4 \quad = \quad W x = - \left( \frac{8}{135} \right) \left( \frac{15}{2} \right) \times 1614 \ cm^{-1} = -0.7166 \ cm^{-1}
\]

\( ^{27} \) According to the phase convention one has to change the sign of \( a \) and \( b \) (cf. Example 2.3).
\[ \gamma_J \tilde{F}(6) B_6^0 = W(1-|x|) = \left( \frac{4}{3\,864\,861} \right) \left( \frac{3465}{4} \right) \times 148\,\text{cm}^{-1} = 0.1327\,\text{cm}^{-1} \]

\[ \frac{x}{1-|x|} = -5.401 \implies x = -0.8438, \quad W = 0.8493 \]

On account of \( W > 0 \) the \( E_{\text{LF}}/W \) axis points upwards. Consequently, the LF ground state at \( x = -0.8438 \) is \( \Gamma_6 \). The corresponding LF state of highest energy is \( \Gamma_8^{(3)} \). The energy separation \( \Delta E_{\text{LF}}/W \) between \( \Gamma_8^{(3)} \) and \( \Gamma_6 \) is 490 cm\(^{-1} \), so that \( \text{CFOS} = \Delta E_{\text{LF}} = 490 \times 0.8493\,\text{cm}^{-1} = 416\,\text{cm}^{-1} \), in agreement with the data given in ref. [26], p. 2591.

8. In which respect does the magnetic susceptibility of a mononuclear lanthanide systems with Ln point symmetry (i) \( O_h \), (ii) \( D_{\infty h} \), (iii) \( D_{2h} \) differ?

(i) \( O_h \): isotropic (cubic) system (\( \chi_x = \chi_y = \chi_z \))

(ii) \( D_{\infty h} \): anisotropic (cylindrical) system (\( \chi_x = \chi_y \neq \chi_z \))

(iii) \( D_{2h} \): anisotropic (orthorhombic) system (\( \chi_x \neq \chi_y \neq \chi_z \))

9. The Bleaney-Bowers formula, eq. (127), approaches at high temperature the Curie-Weiss law \( \chi_m = C/(T - \theta) \). Determine the relation between \( J_{\text{ex}} \) and \( \theta \). Is the result in agreement with the relation \( \theta = (2S(S+1)/3k_B) \sum_i z_i J_{\text{ex},i} \)?

\[
\chi_m = \mu_0 N_A \mu_B g^2 \frac{1}{3k_B T} \left[ 1 + \frac{1}{3} \exp \left( \frac{-2J_{\text{ex}}}{k_B T} \right) \right] \quad (\exp \pm x \approx 1 \pm x \quad \text{for} \quad x \rightarrow 0)
\]

\[
\approx \mu_0 N_A \mu_B g^2 \frac{1}{3k_B T} \left[ 1 + \frac{1}{3} \exp \left( \frac{-2J_{\text{ex}}}{k_B T} \right) \right]
= \frac{\mu_0 N_A \mu_B g^2}{3k_B T} \left( \frac{4}{3} - \frac{2J_{\text{ex}}}{3k_B T} \right)
= \frac{\mu_0 N_A \mu_B g^2}{3k_B} \left( T - \frac{2J_{\text{ex}}}{3k_B} \right)
= \frac{\mu_0 N_A \mu_B g^2}{3k_B} \left( \frac{3}{4} \right)
\]

\[
\theta = \frac{J_{\text{ex}}}{2k_B} \left[ 2S(S+1)/3k_B \right] \sum_i z_i J_{\text{ex},i} = \frac{J_{\text{ex}}}{2k_B} \quad \text{for} \quad S = \frac{1}{2}, i = 1, z_i = 1
\]

10. What magnetic behaviour is obtained, if in the Bleaney-Bowers formula, eq. (127), \( J_{\text{ex}} \) is set to 0?

\[
\chi_m = \mu_0 N_A \mu_B g^2 \frac{1}{3k_B T} \left[ 1 + \frac{1}{3} \exp \left( \frac{-2J_{\text{ex}}}{k_B T} \right) \right]
\]

\[
\overset{J_{\text{ex}} \to 0}{\to} \chi_m = \frac{N_A \mu_B g^2}{3k_B T} \left( \frac{3}{4} \right) \quad \text{Curie law}
\]

11. What are the electronic (4f\(^N \)) and LF symmetrical preconditions for building up a homodinuclear Ln molecule with large \( \mu_{\text{eff}} \) and high magnetic anisotropy?

(i) Ln from the second half of the Ln series (on account of free ion ground states with \( J = L + S \));

(ii) Ln with half-integer \( J \) (nonmagnetic LF ground states of the Ln ion are ruled out);

(iii) Ln with large \( S \) and large \( L \);

(iv) anisotropic LF, for example unique axis anisotropy (cylindrical, hexagonal, tetragonal)
12. Magnetochemical results are often presented as $\chi_m - T$, $\chi_m^{-1} - T$ or $\mu_{\text{eff}} - T$ plots. What type of diagram is suited for molecular systems showing (a) Curie paramagnetism, (b) intramolecular ferromagnetic interactions, (c) intramolecular antiferromagnetic interactions, (d) diamagnetic behaviour, (e) TUP behaviour?

(a) $\chi_m^{-1} - T$  (b) $\mu_{\text{eff}} - T$  (c), (d), (e) $\chi_m - T$

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

To furnish proof of (i) ferromagnetic impurities, (ii) magnetic ordering effects

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

Weak magnetic ordering effects may be overlooked.

15. 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?

Measurement of the magnetic susceptibility of the ligand.

16. For a polynuclear complex one observes at high temperature Curie-Weiss behaviour with $\theta > 0$ and in the low-temperature region field-dependent susceptibilities. What magnetic collective effect can be expected?

Ferromagnetism

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

(i) Intramolecular spin-spin coupling of ferromagnetic nature, intermolecular spin-spin coupling of antiferromagnetic nature.

(ii) Consideration of a molecular field parameter $\lambda_{\text{MF}}$: $\chi_m^{-1} = (\chi'_m)^{-1} - \lambda_{\text{MF}}$

18. You notice that the paramagnetic properties of a homodinuclear molecular compound is not satisfactorily described with the corresponding eq. (128). What simple extensions of the model are in principle possible?

(i) Addition of a TIP term $\chi_0$;

(ii) Consideration of intermolecular exchange interactions by a molecular field parameter $\lambda_{\text{MF}}$. 

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### 6 Appendix 1

#### 6.1 Magnetic quantities

<table>
<thead>
<tr>
<th>Table 33: Definitions, units and conversion factors [5]</th>
</tr>
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<tbody>
<tr>
<td>Quantity</td>
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<tr>
<td>---</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
<td>$\chi$</td>
</tr>
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<tr>
<td>$\chi_m$</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
</tr>
</tbody>
</table>

$^a$ Multiplicative factor applied to the value in CGS-emu units to obtain the value in SI units.

$^b$ H = Henry; H/m = Vs/(Am).

$^c$ $\rho$ = mass density.

$^d$ Specific magnetization; $\sigma^* =$ specific saturation magnetization.

$^e$ $M =$ molar mass.

$^f$ $M_m =$ molar saturation magnetization.

$^g$ $\mu_a =$ atomic magnetic saturation moment.
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., $\mu_{\text{eff}}$ or $\mu_{\text{eff}}^2$ instead of $\chi_m T$.

- Do not mix the systems, e.g., use G (Gauss) instead of T (Tesla) in the CGS-emu system.
- Use $B_0 = \mu_0 H$ in graphical representations (conversion factor $10^{-4}$ T/Oe).

### 6.2 Energy equivalents and conversion factors

#### Tab. 34: Energy equivalents and conversion factors

<table>
<thead>
<tr>
<th></th>
<th>J</th>
<th>eV</th>
<th>s$^{-1}$</th>
<th>cm$^{-1}$</th>
<th>K</th>
<th>T</th>
<th>kJ/mol</th>
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<td>1 s$^{-1}$</td>
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<td>$\times 10^{-11}$</td>
<td>$\times 10^{-13}$</td>
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<td>$\times 10^{-1}$</td>
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<td>$\times 10^{-5}$</td>
<td>$\times 10^{10}$</td>
<td>$\times 10^{10}$</td>
<td>$\times 10^{-1}$</td>
<td>$\times 10^{-3}$</td>
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</tr>
<tr>
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<tr>
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<td>$\times 10^{-5}$</td>
<td>$\times 10^{10}$</td>
<td>$\times 10^{10}$</td>
<td>$\times 10^{-1}$</td>
<td>$\times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>1 kJ/mol</td>
<td>$1.66054 \times 10^{-21}$</td>
<td>$1.03642 \times 10^{-2}$</td>
<td>$2.50607 \times 10^{12}$</td>
<td>$8.35933 \times 10^{12}$</td>
<td>$1.20272 \times 10^{12}$</td>
<td>$1.79053 \times 10^{12}$</td>
<td>$1$</td>
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7 Appendix 2: Matrix elements of operator equivalents

Tab. 35: Matrix elements of the operator equivalents $\tilde{O}_0^4$ [20]

| $J$ | $\tilde{F}(4)^a)$ | $\langle M_J||M_J\rangle$ |
|-----|-----------------|-----------------|
| $\frac{5}{2}$ | 15/2 | 2 \ -3 \ 1 \ - \ - \ - \ - |
| $\frac{7}{2}$ | 15/2 | 9 \ -3 \ -13 \ 7 \ - \ - \ - |
| $\frac{9}{2}$ | 21/2 | 18 \ 3 \ -17 \ -22 \ 18 \ - \ - |
| $\frac{11}{2}$ | 15 | 28 \ 12 \ -13 \ -33 \ -27 \ 33 \ - |
| $\frac{13}{2}$ | 15/2 | 108 \ 63 \ -13 \ -92 \ -132 \ -77 \ 143 \ |
| $\frac{15}{2}$ | 15/2 | 189 \ 129 \ 23 \ -101 \ -201 \ -221 \ -91 \ 273 |

\[ a) \text{ In ref. [20] the respective products } \tilde{F}(4) \times \tilde{O}_0^4 \text{ etc. are listed.} \]

Tab. 36: Matrix elements of the operator equivalents $\tilde{O}_{\pm 4}^4$ [20]

| $J$ | $\tilde{F}(44)$ | $\langle M_J||M_J - 4\rangle$ |
|-----|-----------------|-----------------|
| $\frac{5}{2}$ | $3\sqrt{35}/2$ | $\langle \frac{5}{2}||-\frac{3}{2}\rangle$ |
| $\frac{7}{2}$ | $3\sqrt{35}/2$ | $\langle \frac{7}{2}||-\frac{1}{2}\rangle$ |
| $\frac{9}{2}$ | $21\sqrt{5}/2$ | $\langle \frac{9}{2}||\frac{1}{2}\rangle$ |
| $\frac{11}{2}$ | $3\sqrt{35}$ | $\langle \frac{11}{2}||\frac{3}{2}\rangle$ |
| $\frac{13}{2}$ | $3\sqrt{35}/2$ | $\langle \frac{13}{2}||\frac{5}{2}\rangle$ |
| $\frac{15}{2}$ | $3\sqrt{35}/2$ | $\langle \frac{15}{2}||\frac{7}{2}\rangle$ |

\[ (2||-2) \ (3||-1) \ (4||0) \ (5||1) \ (6||2) \ (7||3) \ (8||4) \]

| 4 | $3\sqrt{35}/2$ | 15 \ 5\sqrt{7} \ 15 \ - \ - \ - |
| 5 | $3\sqrt{35}/2$ | 35 \ 5\sqrt{42} \ 3\sqrt{70} \ 3\sqrt{210} \ - \ - |
| 6 | $3\sqrt{35}/2$ | 70 \ 21\sqrt{10} \ 15\sqrt{14} \ 5\sqrt{66} \ 3\sqrt{55} \ - |
| 7 | $3\sqrt{35}/2$ | 126 \ 70\sqrt{3} \ 5\sqrt{462} \ 15\sqrt{33} \ 5\sqrt{143} \ 1001 \ |
| 8 | $3\sqrt{35}/2$ | 210 \ 6\sqrt{155} \ 15\sqrt{154} \ 5\sqrt{1001} \ 15\sqrt{015} \ 5\sqrt{273} \ 2\sqrt{455} |

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Tab. 37: Matrix elements of the operator equivalents \( \tilde{O}_6^0 \) [20]

| \( J \) | \( \bar{F}(6) \) | \( \langle M_J | M_J \rangle \) |
|---|---|---|
| \( \frac{5}{2} \) | 0 | \( \pm \frac{1}{2} \) \( \pm \frac{3}{2} \) \( \pm \frac{5}{2} \) \( \pm \frac{7}{2} \) \( \pm \frac{9}{2} \) \( \pm \frac{11}{2} \) \( \pm \frac{13}{2} \) \( \pm \frac{15}{2} \) |
| \( \frac{7}{2} \) | 315/4 | -5 | 9 | -5 | 1 | - | - | - | - |
| \( \frac{9}{2} \) | 315 | -8 | 6 | 10 | -11 | 3 | - | - | - |
| \( \frac{11}{2} \) | 945/2 | -20 | 4 | 25 | 11 | -31 | 11 | - | - |
| \( \frac{13}{2} \) | 135 | -200 | -25 | 185 | 227 | -11 | -319 | 143 | - |
| \( \frac{15}{2} \) | 3465/4 | -75 | -25 | 45 | 87 | 59 | -39 | -117 | 65 |

| \( J \) | \( \bar{F}(6) \) | \( \langle M_J | M_J - 4 \rangle \) |
|---|---|---|
| \( \frac{5}{2} \) | 0 | \( \langle \frac{5}{2} | - \frac{3}{2} \rangle \) \( \langle \frac{7}{2} | - \frac{1}{2} \rangle \) \( \langle \frac{9}{2} | \frac{1}{2} \rangle \) \( \langle \frac{11}{2} | \frac{3}{2} \rangle \) \( \langle \frac{13}{2} | \frac{5}{2} \rangle \) \( \langle \frac{15}{2} | \frac{7}{2} \rangle \) |
| \( \frac{1}{2} \) | 45√14/4 | -7√3 | 3√35 | - | - | - | - |
| \( \frac{3}{2} \) | 315√2/4 | -16√3 | 6√2 | 30√2 | - | - | - |
| \( \frac{5}{2} \) | 135√7/2 | -63 | -√105 | 13√21 | 7√165 | - | - |
| \( \frac{7}{2} \) | 135√14/2 | -56√5 | -21√6 | 13√22 | 46√11 | 6√715 | - |
| \( \frac{9}{2} \) | 495√14/4 | -42√15 | -6√231 | 3√77 | 7√429 | 3√5005 | 5√1365 |

| \( J \) | \( \langle 2 | -2 \rangle \) | \( \langle 3 | -1 \rangle \) | \( \langle 4 | 0 \rangle \) | \( \langle 5 | 1 \rangle \) | \( \langle 6 | 2 \rangle \) | \( \langle 7 | 3 \rangle \) | \( \langle 8 | 4 \rangle \) |
|---|---|---|---|---|---|---|---|
| 4 | 135√14/4 | -14 | -√7 | 2√70 | - | - | - | - |
| 5 | 45√14/4 | -168 | -13√42 | 12√70 | 15√210 | - | - | - |
| 6 | 135√14/4 | -168 | -35√10 | 8√14 | 21√66 | 28√55 | - | - |
| 7 | 45√14/4 | -1260 | -546√3 | -6√462 | 147√33 | 126√143 | 45√1001 | - |
| 8 | 495√14/4 | -252 | -6√1155 | -6√154 | 3√1001 | 2√15015 | 19√273 | 12√455 |
References


