Crystal field and spin-orbit interaction

In the solid state, there are two important contributions dominating the spin properties of the individual atoms/ions:

1. Crystal field
   
   The crystal field describes the influence of the surrounding atoms/ions on the electronic energy.

   This method assumes that the atomic/ionic quantum mechanical problem has been solved first. One then calculates the electrostatic interactions of the surrounding sites by perturbation theory.

   The method was put on a quantitative basis by Bethe (1929) and Van Vleck (1932). It is particularly useful for paramagnetic ions in inorganic crystals.

2. Spin orbit interaction
   
   Orbital motion and the magnetic spin moment are coupled via the magnetic interaction of the spin magnetic moment with the magnetic field of the orbital motion. In atoms this interaction has the form: \( \hat{H}_{\text{SO}} = \lambda \cdot \hat{L} \cdot \hat{S} \)
The Hamilton operator of an electron with orbital momentum $L$ and spin momentum $S$ in a magnetic field $B_0$ is:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V_0(r) + V_1(r) + \lambda \cdot \hat{L} \cdot \hat{S} + g_L \cdot \mu_B \cdot B_0 \cdot \hat{L} + g_S \cdot \mu_B \cdot B_0 \cdot \hat{S}$$

Very important for the solution of this Hamiltonian are the relevant energy scales:

<table>
<thead>
<tr>
<th>Energy Scale</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic energy</td>
<td>$1\text{eV} - 10\text{eV}$</td>
</tr>
<tr>
<td>Potential energy $V_0(r)$</td>
<td>$1\text{eV} - 10\text{eV}$</td>
</tr>
<tr>
<td>Crystal field $V_1(r)$</td>
<td>$12.5\text{meV} - 1.25\text{eV}$</td>
</tr>
<tr>
<td>Spin orbit interaction</td>
<td>$1.25\text{meV} - 250\text{meV}$</td>
</tr>
<tr>
<td>Zeeman interaction</td>
<td>$&lt; 1.25\text{meV}$</td>
</tr>
</tbody>
</table>

$$E = 1\text{eV} = h \cdot 241\text{THz} = h \cdot c \cdot 8000\text{cm}^{-1}$$

$$E = h \cdot f = h \cdot c \cdot \frac{1}{\lambda} = h \cdot c \cdot \nu$$
The Zeeman interactions are usually small. Even for $B = 10 \, \text{T}$: 

$$2\mu_\text{B} \cdot B_0 = h \cdot c \cdot 9.29 \, \text{cm}^{-1}$$

The spin orbit interaction in atoms increases with the nuclear $Z$. Typical atomic values are:

$$\hat{H}_\text{SO} = \lambda \cdot \hat{L} \cdot \hat{S} \quad \lambda: \text{spin orbit coupling constant}$$

<table>
<thead>
<tr>
<th>atom</th>
<th>B</th>
<th>C</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>10 cm(^{-1})</td>
<td>28 cm(^{-1})</td>
<td>271 cm(^{-1})</td>
<td>440 cm(^{-1})</td>
<td>1842 cm(^{-1})</td>
</tr>
</tbody>
</table>

From atomic physics: For hydrogen-like wave functions, quantum number $n$: 

$$\lambda \propto \frac{Z^4}{n^6}$$

The crystal field $V_1(r)$ and the spin orbit interaction $\lambda \cdot L \cdot S$ are nearly always (much) larger than the Zeeman interactions $\mu_\text{B} \cdot B_0 \cdot L$ and $2 \cdot \mu_\text{B} \cdot B_0 \cdot L$.

Thus the magnetic moment is always a small perturbation on the electronic problem. The magnetic properties have to be solved by perturbation methods after the solution of the electronic structure.

With respect to the influence of the crystal field and the spin orbit interaction, we have to distinguish between the following cases:
1. Spin orbit interaction « crystal field

\[ \left| \langle \lambda \cdot \hat{L} \cdot \hat{S} \rangle \right| \ll \left| \langle V_1(r) \rangle \right| \]

This is the case for light transition elements like the 3-d elements.

The crystal field problem is solved first, and the spin orbit interaction is treated as a perturbation.

2. Spin orbit interaction » crystal field

\[ \left| \langle \lambda \cdot \hat{L} \cdot \hat{S} \rangle \right| \gg \left| \langle V_1(r) \rangle \right| \]

This is the case for the heavy rare earth elements 4f, 5f.

The states corresponding to the total angular momentum \( \hat{J} = \hat{L} + \hat{S} \) are taken as basis states and the crystal field \( V_1(r) \) is treated as a perturbation.

3. Spin orbit interaction \( \approx \) crystal field

\[ \left| \langle \lambda \cdot \hat{L} \cdot \hat{S} \rangle \right| \approx \left| \langle V_1(r) \rangle \right| \]

\( V_1(r) \) and \( \lambda \cdot \hat{L} \cdot \hat{S} \) have to be diagonalised together.
Case 1:  \[ \left| \langle \hat{\lambda} \cdot \hat{L} \cdot \hat{S} \rangle \right| \ll \left| \langle V_i(r) \rangle \right| \]

We regard an electronic wave function of p-symmetry surrounded by charged ions.

The 4 charges along \( \pm x, \pm y \) set up the crystal field for the electron in the p-functions.

The \( p_x \) orbital will be lowered in energy, due to the vicinity of the positive charges \( +q \) along the \( \pm x \) axes.
The $p_y$ orbital will be shifted up in energy, due to the vicinity of the negative charges $-q$ along the $\pm y$ axes.

The $p_z$ orbital will be unaffected in energy.

Without spin-orbit interaction, the total wave functions would be product wave functions:

Orbital wave function $\cdot$ spin function $u_m$

The energy level diagram is depicted on the right. Each level is doubly degenerate without spin-orbit interaction.
The basis functions with spin \( u_m \) are:

\[
\begin{align*}
&x \cdot f(r) \cdot u_m \\
y \cdot f(r) \cdot u_m & \quad m = 1, 2 \\
z \cdot f(r) \cdot u_m
\end{align*}
\]

\( u_1 = \left| \uparrow \right\rangle \) \hspace{1cm} \( u_2 = \left| \downarrow \right\rangle \)

6 basis functions for the p-orbitals

Spin up, spin down

One now calculates in a perturbation theory the influence of the operators:

\[
\mu_B \cdot B \cdot \hat{L} \quad \lambda \cdot \hat{L} \cdot \hat{S}
\]

Typical matrix elements are:

\[
\begin{align*}
&\int \int x \cdot f(r) \cdot u_m^* \left( \mu_B \cdot B_z \cdot \hat{L}_z \right) \cdot x \cdot f(r) \cdot u_m \cdot \text{d}r \cdot \text{d}\tau_s \\
&\int \int y \cdot f(r) \cdot u_m^* \left( \lambda \cdot \hat{L}_z \cdot \hat{S}_z \right) \cdot y \cdot f(r) \cdot u_m \cdot \text{d}r \cdot \text{d}\tau_s
\end{align*}
\]

\( \text{d}r \): integration over the spatial coordinates

\( \text{d}\tau_s \): integration over the spin degree of freedom

\[
\begin{align*}
&\int x \cdot f(r) \cdot \hat{L}_z \cdot x \cdot f(r) \cdot \text{d}r = 0 \\
&\int y \cdot f(r) \cdot \hat{L}_z \cdot y \cdot f(r) \cdot \text{d}r = 0 \\
&\int z \cdot f(r) \cdot \hat{L}_z \cdot z \cdot f(r) \cdot \text{d}r = 0
\end{align*}
\]

All diagonal matrix elements of the orbital operators vanish! This is termed:

quenching of orbital angular momentum.

Proof: e.g. Slichter p.89 ff
After a rather lengthy calculation (see details e.g. in Slichter p. 505 – 516) one arrives at an effective spin Hamiltonian operator:

\[
\hat{H} = \mu_B \cdot (g_{xx} B_x \hat{S}_x + g_{yy} B_y \hat{S}_y + g_{zz} B_z \hat{S}_z )
\]

- \(g_{xx} = 2\)
- \(g_{yy} = 2 \cdot (1 - \frac{\lambda}{E_z - E_x})\)
- \(g_{zz} = 2 \cdot (1 - \frac{\lambda}{E_y - E_x})\)

Electron is in the state \(x \cdot f(r)\) !!

"circulation" via \(p_z, p_x\)

"circulation" via \(p_y, p_x\)

The main effect is a g-shift proportional to the spin-orbit interaction \(\lambda\) and inversely proportional to the energy difference of the higher lying state.

Let \(E_y - E_x \approx 10000\text{ cm}^{-1}\), \(\lambda \approx 100\text{ cm}^{-1}\)

\[g_{zz} = 2 \cdot (1 - 10^{-2}) : 1\%\text{ effect!}\]

Note: The electron with this g-tensor is in the lowest energy eigenstate, which is the \(p_x\)-state!
By "circulation" via the excited state $p_z$ at $\Delta E = E_z - E_x$:

$$p_{x^+} - p_{z^+} - p_{x^-} - p_{z^-}$$

$$g_{yy} = 2 \cdot \left( 1 - \frac{\lambda}{(E_z - E_x)} \right)$$

$B_x$: field is along the occupied $p_x$ state.

$$g_{xx} = 2$$

By "circulation" via the excited state $p_y$ at $\Delta E = E_y - E_x$:

$$p_{x^+} - p_{y^+} - p_{x^-} - p_{y^-}$$

$$g_{zz} = 2 \cdot \left( 1 - \frac{\lambda}{(E_y - E_x)} \right)$$
General structure of the g-shift:  correction term $\propto \frac{\lambda}{\Delta E}$

$\Delta E$ is the energy distance to a state near the occupied state.

This scheme can even be applied to extended electron states in a semiconductor band structure. The g factor $g_c$ of the conduction electrons in III-V semiconductors like GaAs, InSb, InP, GaN etc. can be calculated by a model termed $k\cdot p$ theory.

The essential parameters are again the spin-orbit coupling $\Delta_0$ and the energy difference $E_g$.

Since band electrons have an effective mass $m_{\text{eff}}$, this is another parameter.

$$g_c = 2 \cdot \left[1 - \left(\frac{m_0}{m_{\text{eff}}} - 1\right) \cdot \frac{2 \cdot \Delta_0}{3 \cdot E_g + 4 \cdot \Delta_0}\right]$$

GaAs:  $g_c \approx -0.44$

InSb:  $g_c \approx -50$
Crystal field for d-electrons,
case of transition elements on lattice sites of e.g. semiconductors, insulators.

The example with the p-electron is not often encountered in real solids, since the p-electrons participate very strongly in chemical bonds. What is very common, however, is the case of d-electrons in solids. Many transition element ions can be built into solids on lattice sites (with the appropriate ionic charge). Or these transition elements form complexes with high symmetry.

We examine the case of octahedral symmetry and the case with a small tetragonal distortion from octahedral symmetry.
The 5 d orbitals ($d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{3z^2-r^2}$) have different interactions with the dipole fields from the $\text{H}_2\text{O}$ molecules. This is due to the directions into which the lobes of these orbitals point.

Energy splitting by the cubic field

\[ d_\gamma \]

\[ d_\varepsilon \]
Very often, one has a tetragonal distortion of the complex, e.g. a slight movement of the H$_2$O molecules along the ±z axis.

This leads to an additional splitting of the $d_\gamma$ and $d_\varepsilon$ states.

The ground state is a single level, and thus a spin doublet.

It can be split by a magnetic field.
The g-tensor values for the ground state are:

\[ g_x = g_y = g_e - 2 \cdot \frac{\lambda}{\delta} \]
\[ g_z = g_e - 8 \cdot \frac{\lambda}{\Delta} \]

This is an axial tensor.

For KTi(C_2O_4)_2·2H_2O the relevant ion is Ti^{3+}:

\[ g_x = g_y = 1.96 \]
\[ g_z = 1.86 \]
\[ \lambda = 154 \text{ cm}^{-1} \]
\[ \delta = 7700 \text{ cm}^{-1} \]
\[ \Delta = 8800 \text{ cm}^{-1} \]