Angular Momentum and Magnetic Moment

Electrons that perform a circular movement with an angular momentum \( l \) have a magnetic dipol moment \( \mu_l \):

\[
\mu_l = -\gamma l \quad \text{where} \quad \gamma = \frac{e}{2m_e}
\]

\( \gamma \) is called the gyromagnetic constant. The magnetic moment is usually refered to in units of Bohr’s magneton \( \mu_B \):

\[
\mu_l = -\frac{\mu_B l}{\hbar} \quad \mu_B = 9.27402 \times 10^{-24} \text{ J/T}
\]
Schroedinger Equation

- **Quantization** of Spin and Angular Momentum

\[ |j| = \hbar \sqrt{l(l + 1)} \]

\[ l_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \ldots, \pm l \]

\[ |s| = \hbar \sqrt{s(s + 1)} \]

\[ s_z = m_s \hbar \quad m_s = \pm s \]

\[ \mu_s = -\frac{g_e \mu_B s}{\hbar} \]

- Landé factor

\[ g_e = 2.00232 \]
Theory

- Interaction of the Electron with an External Magnetic Field

\[ E = -\mu_i B \cos \alpha \]

\( \mu_i \) aligns with respect to the axis of the external magnetic field (z)
→ Precission of \( \mu_i \) along \( z \)
→ Quantization of \( \alpha \)
  \( (\alpha = \text{angle between } \mu_i \text{ along } z) \)
Russel-Saunders (LS) Coupling

- **Fine Structure of Atoms**
  For atoms in the gas phase of light elements, the total angular ($L$) and spin ($S$) momenta couple to give a total momentum ($J$) and a corresponding magnetic moment $\mu_j$:

  \[ \mu_j = -g_j \frac{e}{2m_e} J \]

  where $J = |L + S|, \ldots, |L - S|$.

This generates the so-called fine structure in the electronic spectra of atoms.
Zeeman Effect

- Interaction of the magnetic moment $\mu_J$ with the external field lifts the energetic degeneracy of the $(2J + 1)$ electronic $M_J$ states.

- Magnitude of energetic splitting depends linearly on the magnetic field strength.
  
  - Electron Paramagnetic Resonance: transitions between the magnetically split $M_J$ levels.
  
  - Frequencies in the microwave region.
  
  - Selection rule: $\Delta J = 0$, $\Delta M_J = \pm 1$.

  $\Delta E = h\nu = g_J \mu_B B$
Example

- $^{16}$O-Atom: $l = 1$, $s = 1$ ($J = 2, 1$)

\[
\begin{align*}
\text{3P}_1 & \quad \text{M}_J \\
1 & \\
0 & \\
-1 & \\
\text{3P}_2 & \quad \text{M}_J \\
2 & \\
1 & \\
0 & \\
-1 & \\
-2 &
\end{align*}
\]
Hyperfine Splitting

- Interaction of the magnetic moment of the electron with that of the nucleus (angular momentum: \( I \)).
- Requirement: \( I \neq 0 \).
- The hyperfine splitting constant \( a \) is easily obtained from the spectra:

\[
S = \frac{1}{2} \\
I = \frac{3}{2}
\]

\[
a = \frac{\Delta B g_j \mu_B}{h}
\]
g shifts

- For atoms in the gase phase, the g value is simply defined as:

\[ g = 1 + \frac{[J(J + 1) + S(S + 1) - \Lambda(\Lambda + 1)]}{2J(J + 1)} \]

- Experimentally, this value is accessible from the spectra:

\[ B = \frac{h\nu}{\mu g} \]

- g factors are characteristic for the angular momentum J of the atom and hence, allow for the easy determination of this value experimentally (compare to d in NMR)
Example

Spectrum von NO.

7232.80 G

20 G
Example: NO

\[ ^2\Pi_{3/2} \]

\[ M_J \]

\[ M_I \]

\[ 3/2 \]

\[ 1/2 \]

\[ -1/2 \]

\[ -3/2 \]

\[ 1/2 \ a \]

\[ 3/2 \ a \]

\[ \Delta M_J = \pm 1 \]

\[ \Delta M_I = 0 \]

\[ ^{16}\text{O}, \ I=0 \]

\[ ^{14}\text{N}, \ I=1 \]

\[ L=0 \]

\[ S=3/2 \]

\[ J=3/2 \]

\[ a=32,63 \text{ MHz} \]

\[ g_J=0,7759 \]
Example: Organic Radical

$^{31}\text{P}$, $I=1/2$

$^1\text{H}$, $I=1/2$

$^{11}\text{B}$, $I=3/2$

EPR spectrum of $(\text{MeO})_3\text{PBH}_2$: 21 lines!!
Spin-Only Approximation

- In molecules with more than 2 atoms, especially in coordination compounds, the ground state is usually non-degenerate (Jahn-Teller Effect)
  \[ \rightarrow L = 0!! \text{ (but excited states can be degenerate) } \]

Examples for Jahn-Teller active electron configurations:
g Anisotropy in Coordination Compounds

- The anisotropy of g values in coordination compounds is due to spin-orbit coupling
  \[ g_x \neq g_y \neq g_z \]
- From perturbation theory, the g values are calculated:

\[
g_i = g_e - 2\lambda \sum_{n \neq 0} \frac{\langle \Psi_0 | L_i | \Psi_n \rangle \langle \Psi_n | L_i | \Psi_0 \rangle}{E_n - E_0}
\]

- Example: spin-orbit coupling similar in x and y direction, but different in z:
  \[ g_x = g_y (g_{\perp}) \neq g_z (g_{\parallel}) \]
The Instrument

- **Design of an EPR Spectrometer**

EPR transitions:

\[ \Delta E = h\nu = g\mu_B B \]
Example: tetragonal $[\text{CuCl}_4]^{2-}$

$X^2 - Y^2$

$Z^2$

$xz, yz$

$xy$

Ground State: $^2B_{1g}$

$$g_i = g_e - 2\lambda \sum_{n \neq 0} \frac{\langle \Psi_0 | L_i | \Psi_n \rangle \langle \Psi_n | L_i | \Psi_0 \rangle}{E_n - E_0}$$

$$g_z = ? \quad \rightarrow \quad L_z$$

Effect of $L_i$ on real $d$ orbitals:

<table>
<thead>
<tr>
<th>$\hat{L}<em>x d</em>{xz}$</th>
<th>$\hat{L}<em>y d</em>{xz}$</th>
<th>$\hat{L}<em>z d</em>{xz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-i d_{xy}$</td>
<td>$i d_{x^2-y^2} - i\sqrt{3} d_{z^2}$</td>
<td>$i d_{yz}$</td>
</tr>
<tr>
<td>$i\sqrt{3} d_{yz} + i d_{x^2-y^2}$</td>
<td>$i d_{xy}$</td>
<td>$-i d_{xz}$</td>
</tr>
<tr>
<td>$i d_{xz}$</td>
<td>$-i d_{yz}$</td>
<td>$-2i d_{x^2-y^2}$</td>
</tr>
<tr>
<td>$-i d_{yz}$</td>
<td>$-i d_{xz}$</td>
<td>$2i d_{xy}$</td>
</tr>
<tr>
<td>$-i\sqrt{3} d_{yz}$</td>
<td>$i\sqrt{3} d_{xz}$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

Only one contribution!
Example: tetragonal $[\text{CuCl}_4]^{2-}$

Ground State: $^2\text{B}_{1g}$

$$g_i = g_e - 2\lambda \sum_{n \neq 0} \frac{\langle \Psi_0 | L_i | \Psi_n \rangle \langle \Psi_n | L_i | \Psi_0 \rangle}{E_n - E_0}$$

- $g_z = g_{\parallel} = 2.023 - 8\lambda / E(x^2-y^2) - E(xy)$
- $g_{x,} = g_{\perp} = 2.023 - 2\lambda / E(x^2-y^2) - E(yz)$
- $g_{y,} = g_{\perp} = 2.023 - 2\lambda / E(x^2-y^2) - E(xz)$

Two transitions!
Example: tetragonal $[\text{CuCl}_4]^{2-}$

$g_{\parallel} = 2.22$ 

$g_{\perp} = 2.04$ 

Cu: $I = 3/2$
Example: low-spin ferric heme

Relevant for Cytochrome C

Rhombic
- g-values: 2.8, 2.3, 1.6
- Parallel IM orientation

Large $g_{\text{max}}$
- g-values: 3.4 (1.8, 0.9)
- Perpendicular IM orientation

Axial
- g-values: 2.2, 1.94
- ?
$S > \frac{1}{2}$: Zero-field splitting

- Example: high-spin Fe(III)
S > ½: Zero-field splitting

Solomon et al., *Chemistry & Biology*, 1997, 4, 795-808