% Electron Paramagnetic Resonance (EPR) Spectroscopy
(a.k.a. ESR, EMR)

Lecture VI. More than one unpaired electron, \( S > \frac{1}{2} \) (1)

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Interaction between two unpaired electrons \( s = \frac{1}{2} \)

\( \rightarrow \) total spin states \( S = 0 \) and \( 1 \)

- States are separated in energy by the isotropic exchange parameter, \( J \)
- When \( J \) is very small, comparable to the hyperfine interaction, \( A \); referred to as bi-radicals
- Form of fluid spectra depends on magnitude of \( J \) versus \( A \)

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More than one unpaired electron in degenerate orbitals

- Electron 1: \( s_1 = \frac{1}{2} \)
- Electron 2: \( s_2 = \frac{1}{2} \)

Define a total spin \( S \) with possible values \( s_1 + s_2 \) and \( s_1 - s_2 \)

- Hund's rule: ground state has maximum \( S \)
- \( S = 1 \) and \( 0 \): a spin triplet and spin singlet.

- \( S = 0 \) and \( 2J \): EPR active
- Differ in energy because of differing electron-electron repulsions.
- Repulsion less in triplet \( \Rightarrow \) Hund's rule
- Quantified by the exchange constant \( J \)
- \( J > 10^3 \text{ cm}^{-1} \) for electrons on same paramagnetic centre.
- For EPR can consider as isolated \( s = 1 \)
More than one unpaired electron: $S = 1$

- Now have to consider e-e interactions (usually $\gg$ e-n).
- $\rightarrow$ zero-field splitting, $D$
- New Zeeman diagram…

In general, 2$S$ allowed transitions per orientation: fine structure.

Spectra spread over much larger field ranges

Zero-Field Splitting

- Two mechanisms:
  (i) Dipolar e-e interaction ($\propto 3\cos^{2}\theta$-1). Dominant for organics
  (ii) Spin-orbit coupling. Dominant for transition ions

- Anisotropic: have $D_x$, $D_y$, and $D_z$ parameters
- If purely dipolar then: $D_x + D_y + D_z = 0$
  (hence no fine structure in fluid solution)

- …then only two independent parameters and can define…

ZFS parameters, $D$ and $E$:

<table>
<thead>
<tr>
<th>Axial term</th>
<th>Rhombic term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D = D_z - (D_x + D_y)/2$</td>
<td>$E = (D_z - D_y)/2$</td>
</tr>
</tbody>
</table>

- Symmetry: isotropic ($D = E = 0$), axial ($D \neq 0$, $E = 0$), rhombic ($E \neq 0$).

$s = 1$, axial symmetry, road map and powder spectrum:

In general for $s > 1/2$, cannot derive analytical expression for resonance fields at arbitrary orientation. Need to diagonalise matrix at each $\theta, \phi$.

$s = 1$ in zero field.

- $E$ mixes states differing by $\Delta M_S = \pm 2$, and breaks degeneracy
- Can define "rhombicity", $\lambda = |E/D|$
- $\lambda = 0$ (axial) to $1/3$ (rhombic limit)
- $\lambda > 1/3 \Rightarrow$ redefinition of axes
\[ s = 1, \text{effect of } E \neq 0 \]
\[
D = D_{zz} - (D_{xx} + D_{yy})/2
\]
\[
E = (D_{xx} - D_{yy})/2
\]

Special cases:
\[ E = 0 \Rightarrow D_{xx} = D_{yy} \neq D_{zz} \]
\[ E/D = 1/3 \Rightarrow D_{yy} = -D_{xx}, D_{zz} = 0 \]

\[ 0 \leq |E/D| \leq 1/3 \text{ by convention} \]

**ZFS for some organic spin triplets**
- Examples are excited state aromatics or ground state carbenes
- \( D \) arises from:
  - Dipolar interaction \( D \propto r^{-3} \) (dominant in organic radicals)
  - and/or
  - Spin-orbit coupling (dominant in transition metals)

**Electron Paramagnetic Resonance (EPR) Spectroscopy**
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Lecture VII. More than one unpaired electron, \( S > \frac{1}{2} \) (2)
\( s = 1 \), some examples: ground state and excited state triplets

\[ \begin{align*}
\sigma^+ & \rightarrow \sigma^- \\
\pi & \rightarrow \pi^* \\
\theta & \neq 0^\circ
\end{align*} \]

\[ \begin{align*}
\Delta m = \pm 2 & \text{ Forbidden} \\
\Delta m = \pm 2 & \text{ transition becomes allowed by field (or } E \text{) induced scrambling of } m \text{ states}
\end{align*} \]

\( s = 1 \), the “half-field” resonance.

\[ \begin{align*}
\Delta m & = \pm 2 \\
\theta & = 0^\circ \\
\theta & = 0^\circ
\end{align*} \]

\( \theta \neq 0^\circ \)

\[ \begin{align*}
|+1> & + |-1> + |0> \\
|+1> & + |-1> + |0>
\end{align*} \]

\[ \begin{align*}
d|+1> + e|-1> + f|0> \\
g|+1> + h|-1> + i|0>
\end{align*} \]

\( \Delta m = \pm 2 \)

Sign of \( D \) from variable temperature behaviour

\[ \begin{align*}
\Delta m = \pm 2 & \text{ Forbidden} \\
\Delta m = \pm 2 & \text{ transition becomes allowed by field (or } E \text{) induced scrambling of } m \text{ states}
\end{align*} \]

\( s = 1 \): Effect of \( h\nu \) vs. \( D \)

\[ \begin{align*}
X\text{-band: } & 9.5 \text{ GHz } = 0.32 \text{ cm}^{-1} \\
g_{iso} & = 2.0, E = 0
\end{align*} \]

\[ \begin{align*}
D / \text{cm}^2 & = 0.05 \\
D & < h\nu \\
D & > h\nu
\end{align*} \]

\[ \begin{align*}
D & < h\nu \\
D & > h\nu
\end{align*} \]

\( D >> h\nu \text{ might not see spectrum!} \)
**s = 1: Effect of hv vs. D**

- Typical X-band field range
- X-band: 9.5 GHz
- W-band: 95 GHz
  - hv = 0.32 cm⁻¹
  - hv = 3.2 cm⁻¹

**s = 1, example: 6-coordinate Ni²⁺ (d⁸)**

- Typical X-band: 9.5 GHz
- W-band: 95 GHz
  - hv ≈ 3.2 cm⁻¹
  - hv ≈ 0.32 cm⁻¹

From JCS Faraday Trans. 1998, 94, 3019

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**Summary and generalising to s > ½:**

- Spin s has 2s+1 degeneracy: m = +s, +s-1, ..., -s.
- Degeneracy lifted in zero-field by ZFS (D and E)
- In high-field limit (D ≪ hv or gμBH)
  - get 2s EPR transitions per orientation w.r.t. H
- H || z: transitions separated by 2|D|/gμB in field units.
- For axial systems (E = 0),
  - H || x(y): transitions separated by |D|/gμB in field units.

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**Form of S > ½ spectra when hv >> D**

- Quantum number S is associated with 2S + 1 Mₛ states
- -S to +S
- ΔMₛ = ±1
- gives 2S transitions at any orientation
- Number of transitions → S
- Separations → D

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For example: \( s = 3/2; m \pm 3/2, \pm 1/2 \) (spin quartet)

Zero-field energy matrix \(|m\rangle\) basis):

\[
\begin{pmatrix}
|+3/2\rangle & |-1/2\rangle & |+1/2\rangle & |-3/2\rangle \\
D & \sqrt{3}E & 0 & 0 \\
\sqrt{3}E & -D & 0 & 0 \\
0 & 0 & -D & \sqrt{3}E \\
0 & 0 & 0 & D \\
\end{pmatrix}
\]


\( E \) mixes \( \Delta m \pm 2 \), as before

\[ \Rightarrow \text{two-fold degeneracy retained in zero-field even with} E \neq 0 \text{ (Kramers' theorem)} \]

\( s = 3/2, D \gg h\nu \): effective \( g \)-values

- \( g_{\text{eff}} \) are very sensitive to \( E/D \), hence can use them to determine this ratio (including sign) even when you cannot determine \( D \) or \( E \! \)

- If \( E \neq 0 \) (or \( \theta \neq 0 \)) then mixing can allow transitions within \( "m" = \pm 3/2 \) doublet

- Example, distorted tetrahedral \( \text{Co}^{2+} \) compound (high spin \( d^7 \))...

\[ g_{\text{eff}} \approx 7.4, 1.1, 0.87 \]

\[ E/D = -0.16; D < -15 \text{ cm}^{-1} \]

- See Pilbrow, J. Magn. Reson. 1978, 31, 479 for thorough discussion of \( g_{\text{eff}} \) for \( s = 3/2, 5/2 \)
Electron Paramagnetic Resonance (EPR) Spectroscopy
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Lecture VIII. The anomalous paramagnetism of copper acetate

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“Anomalous paramagnetism and exchange interactions in copper acetate”,
“The paramagnetic resonance spectrum is found to resemble that of a nickel Tutton salt...S = 1.”

\[ S = 1 \]
\[-2J \approx 300 \text{ cm}^{-1} \]

\[ \text{[Cu}_2(O_2CMe)_4(H_2O)_2] \]
\[ S = 0 \]

-EPR proved structure was dimeric.

“EPR spectrum due to triplet population
-Intensity decreases with T \( \Rightarrow \) antiferromagnetically coupled
-\( g_x > g_y \) (square planar Cu\(^{2+}\))

Magnetic properties of copper acetate

Variation of \( \chi_T \) vs \( T \) for Cu\(_2\)(OAc)\(_4\).2H\(_2\)O
Antiferromagnetic coupling
\( S = 0 \) ground state