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

Lecture I. Basic principles of EPR spectroscopy

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Electron Paramagnetic Resonance (EPR) Spectroscopy

-The electron spin equivalent of NMR
-Requires unpaired electrons ($S \geq \frac{1}{2}$)
-Information on the environment of the unpaired electron $\rightarrow$ electronic structure, geometric structure, physical properties, reactivity, dynamics, etc.

EPR transition = flipping the electron spin. E.g. for $S = \frac{1}{2}$...

The resonance condition

$$E = m_S \beta e H$$

$$g \nu \beta e H_{res}$$

$$g = \frac{h \nu}{\beta e H_{res}}$$

$$= 714.5 \frac{\nu \text{ (GHz)}}{H_{res} \text{ (G)}}$$

$g = \frac{h \nu}{\beta e H_{res}}$

$\nu$ = Planck’s constant $= 6.626 \times 10^{-34}$ J s

$\beta e$ = Bohr magneton $= 9.274 \times 10^{-24}$ J T$^{-1}$

$H_{res}$ = 4.668 x 10$^{-5}$ cm$^2$ G$^{-1}$
Frequency vs. Field

- Microwaves appropriate for convenient lab magnets
- Can use different fixed frequencies.
- Advantages to both up- and down-frequency/field

<table>
<thead>
<tr>
<th>Frequency band</th>
<th>ν / GHz</th>
<th>Hres / G for $g_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>4.0</td>
<td>~1400</td>
</tr>
<tr>
<td>X (most common)</td>
<td>9.0</td>
<td>~3200</td>
</tr>
<tr>
<td>Q</td>
<td>34</td>
<td>~12000</td>
</tr>
<tr>
<td>W</td>
<td>94</td>
<td>~33000</td>
</tr>
</tbody>
</table>

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

Lecture II. Isotropic (fluid solution) spectra

The g-value

- Free electron: $g_e = 2.002319…$ a fundamental constant, related to the magnetic moment of the electron due to its spin (ang. mom.). [Nb: gyromagnetic ratio $γ_e = g_e β_e / h$; magn. mom., $μ_e = -g_e β_e √S(S+1)$]

- In real materials, measured $g ≠ g_e$.

  $g ∝ 1/H_{res} ⇒$ higher $g$ at lower field.

  - ...because of orbital angular momentum contribution to the magnetic moment.
  - Can be:
    (i) Ground state (T or E terms) → large orbital moment; need to treat spin-orbit split states. Complicated, and won’t consider further here.

  $e.g.$ $O_6$ Co$^{2+}$; 4T

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Lecture II. Isotropic (fluid solution) spectra

The g-shift

(ii) Mixing with excited states via spin-orbit coupling (SOC) → small orbital moment $∝ 1/ΔE$.

$g ∝ g_e$ for orbital singlets (A or B terms). Normal range $3 > g > 1$.

Often discussed as the g-shift:

$$Δg = g - g_e$$

$λ =$ SOC constant - larger for heavier elements.

$a^2$ ($≤ 1$) = covalency parameter

$n =$ quantum mechanical coefficient
**Trends in g-shift**

\[ g = g_e - \frac{a^2 n \lambda}{\Delta E} \]

Consequently:

(i) Organic free-radicals: usually large \( \Delta E \) (colourless), small \( \lambda \).
- Hydrocarbon radicals \( g \approx 2.002-2.003 \)
- N/O-based radicals \( g \approx 2.003-2.006 \)
- S-based radicals \( g \approx 2.007-2.010 \)

(ii) Transition metal ions: small \( \Delta E \) (coloured; crystal field splittings), big \( \lambda \) \( \rightarrow \) \( g \) significantly different from \( g_e \).

(iii) \( g \) can be < or > \( g_e \).
- Coupling with filled orbital \( \rightarrow +ve \) contribution to \( \Delta g \).
- Coupling with empty orbital \( \rightarrow -ve \) contribution to \( \Delta g \).

  - e.g. \( \{VIVO\}_2^+ \), \( d^1 \) typical \( g \approx 1.9 \)
  - e.g. \( \text{Cu}^{2+} \), \( d^9 \) typical \( g \approx 2.1 \)

**Hyperfine Coupling**

- If electron spin interacts with nuclear spin (I)
  \( \rightarrow \) hyperfine structure, with coupling constant \( A \) (or \( a \)).

- Analogous to nuclear spin-nuclear spin (J) coupling in NMR.

  - 2nd selection rule: \( \Delta m_I = 0 \)
  - Each transition corresponds to a given value of \( m_I \)

  \( \rightarrow 2I+1 \) transitions.

**Coupling Patterns**

- Coupling to \( n \) equivalent spin I nuclei \( \rightarrow 2nI+1 \) multiplet.

- Relative intensities from triangles or stick spectra (as for NMR).

  - E.g. for coupling to \( n \) equivalent \( I = \frac{1}{2} \) nuclei…Pascal’s triangle

  - "add up \( 2I + 1 \) numbers to obtain the next row"

  \[
  \begin{array}{ccccccc}
  n & 0 & 1 & 0 & & & \\
  0 & 1 & 0 & & & & \\
  1 & 0 & 1 & 1 & & & \\
  2 & 1 & 3 & 3 & 1 & & \\
  3 & 1 & 6 & 10 & 5 & 1 & \\
  4 & 1 & 10 & 20 & 15 & 6 & 1 \\
  5 & 1 & 15 & 35 & 35 & 21 & 7 & 1 \\
  6 & 1 & 21 & 56 & 70 & 56 & 28 & 8 \\
  7 & 1 & 28 & 70 & 70 & 56 & 28 & 8 \\
  8 & 1 & 36 & 96 & 126 & 126 & 96 & 36 \\
  \end{array}
  \]

**Triangles for I > 1/2 nuclei**

- \( n \times (I = 1) \); add up \( 2I + 1 = 3 \) numbers

- \( n \times (I = 3/2) \); add up \( 2I + 1 = 4 \) numbers

- \( n \times (I = 5/2) \); add up \( 2I + 1 = 6 \) numbers

Can observe coupling to quadrupolar nuclei, even if in low symmetry
Methyl radical

\[ \text{CH}_2 \text{H} \times 2 \] doublet of 1:3:3:1 quartets

\[ \text{a}_H, \text{a}_C \]

\[ ^{13}\text{C}, 1.1\% \text{ nat. ab., } I = \frac{5}{2} \]

2,2-diphenyl-1-picrylhydrazyl (dpph)

\[ ^{14}\text{N}, 100\% \text{ nat. ab., } I = 1 \]

Two very similar couplings

1:2:3:2:1 pentet

\[ \text{g} = 2.00354 \]

Used as a standard for g-value calibration

[VO(acac)\textsubscript{2}]: V\textsuperscript{IV}, d\textsuperscript{1}

\[ ^{51}\text{V}, 100\% \text{ nat. ab., } I = \frac{7}{2} \]

- "short+fat" and "tall+thin" lines due to tumbling effects. Analysis → rotational correlation times (hence mobility etc)
- note 2\textsuperscript{nd} order effects: separations not even; g offset from centre.

\[ \text{g} = 1.970 \]

[Cu(acac)\textsubscript{2}]: Cu\textsuperscript{II}, d\textsuperscript{9}

\[ ^{65}\text{Cu} 31\% \text{ nat. ab.} \]

\[ ^{63}\text{Cu} 69\% \text{ nat. ab.} \]

Both I = 3/2

- Same g, different A

\[ \frac{A(^{63}\text{Cu})}{A(^{65}\text{Cu})} = \text{ratio of nuclear magnetic moments } (g_n\beta_n I) \text{ hence nuclear } g_n\text{-values} \]

\[ = 1.484/1.588 = 0.935 \]
Other poly-isotopic examples

Each Pt satellite has $^{195.5}_{195}$Pt, I = 1/2, 34% intensity relative to the Z = 0 line.

Each Mo satellite has $^{95.9}_{95}$Mo, I = 5/2, combined 26% intensity.

Superhyperfine" = ligand hyperfine

1:1:1 triplet from $^{14}$N

$[^{195}Cr(CN)]^{3-}$
$^{57}$Cr, I = 3/2, 10%
$^{14}$N, I = 1, 100%

- Unpaired electron must be partly delocalized out to $^{14}$N nucleus.
- Superhyperfine coupling is direct evidence for covalency in coordination compounds.

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Lecture III. Meaning of hyperfine interaction

Units for hyperfine coupling

- Measured in field units, but coupling constant is an interaction energy
- Need to convert to energy (or equivalent) units…

Conversion from field to energy units depends on the $g$-value

\[
g_{iso} = 2.00
\]

\[
A_{res} = 100 \text{ Gauss}
\]

\[
\Delta E = h \nu = g_{iso} \beta_e H_{res}
\]

\[
A(\text{cm}^{-1}) = g \times \beta_e \times A(G)
\]

\[
A(\text{MHz}) = g \times A(G) / 0.7145
\]

From: $\nu = 4.66858 \times 10^{-8}$ cm$^{-1}$ G$^{-1}$

$\beta_e$ in cm$^{-1}$ G$^{-1}$

$A$ in MHz
**Hyperfine (e-n) Mechanisms**

- **Dipolar** (through space): Depends on e-n distance and orientation w.r.t. applied field.
  \[ A_{\text{dip}} \propto 3\cos^2\theta - 1 \]
  - Averages to zero in fluid solution.

- **Spin density at the nucleus (Fermi contact):** Direct contribution only possible if up e is (at least partly) in an s-orbital (p,d,f orbitals have nodes at the nucleus).

- **Spin-orbit coupling** \( \propto \Delta g \): important for d-block

  \Rightarrow\text{Should only see s-electron density in solution, but…}

**Spin Polarisation**

- Unpaired electron interacts differently with the \( \uparrow \) and \( \downarrow \) electrons in a filled orbital
  \( \Rightarrow \) the paired electrons have slightly different spatial distributions.

  \[ \pi(p_z), \sigma(C-H) \]

- Slightly favoured by spin correlation (cf. Hund’s rule)
- “excess” spin up at C; spin down at H – including nucleus.

- Or, configuration interaction between \( p_z^1 \sigma^2 \) with excited states
- Similar arguments for observation of \( ^{13}\text{C} \) splitting or, e.g., metal hyperfine in d-block complexes

**Methyl radical**

- Often see solution hyperfine where symmetry should preclude it!

**McConnell analysis**

Calculation of spin population of \( 2p_z \) orbital in \( \pi \)-radical from hyperfine coupling to bound H

\[ \alpha_{\text{iso}} = \rho Q \]

- Spin density in C \( 2p_z \) orbital
- \( \rho = 1, \ Q = 23 \text{ G} \)

\[ 1:6:15:20:15:6:1 \text{ septet} \]

- \( ^{13}\text{C} \) splitting or, e.g., metal hyperfine in d-block complexes

\[ \rho = 3.75, \ Q = \frac{3}{23} \text{ G} \]

\[ 1:6:15:20:15:6:1 \text{ septet} \]
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Lecture IV. What happens when we immobilise the sample?

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Sample phase and orientation
• in fluid solution molecules tumbling rapidly (mostly) on timescale of experiment.
• Magnetic field “sees” average orientation of the molecule.
  → “isotropic” spectrum.
• …but molecules are not, in general, isotropic. They look different from different orientations.
• As with ALL spectroscopies, spectrum depends on the orientation of the molecule (e.g. polarisation of optical transitions). EPR easy to measure on powders, single crystals, frozen solutions etc.

  • e.g. sq. planar CuII (D_{4h})
  • g and A will depend on orientation of molecule (can define by C_4) w.r.t. H.

  g anisotropy
• Remember $g \neq g_e$ due to excited state orb. ang. mom. via SOC.
• Different excited states contribute to magnetic moment (hence g) in different orientations. Easiest to see by example.

  • Consider a square planar Cu(II) complex, D_{4h} symmetry.
Hand-wavey approach

- Non-zero orbital angular momentum if orbitals can be transformed by rotation about an axis. E.g…

(i) \(x^2-y^2\) transforms to \(xy\) via \(R_z\)

\[
\begin{align*}
\begin{array}{c}
\begin{tikzpicture}
\node (x) at (0,0) {\(x\)};
\node (y) at (0,1) {\(y\)};
\draw[->] (x) -- (y);
\end{tikzpicture}
\end{array}
\rightarrow
\begin{array}{c}
\begin{tikzpicture}
\node (x) at (0,0) {\(x\)};
\node (y) at (0,1) {\(y\)};
\draw[->] (x) -- (y);
\end{tikzpicture}
\end{array}
\end{align*}
\]

\[
\therefore \text{ contribution to magn. moment along } z \text{ from } xy \text{ excited state}
\]

\[
\begin{align*}
\therefore \text{ contribution to magn. moment along } z \text{ from } xy \text{ excited state}
\end{align*}
\]

- SOC along \(x\) or \(y\) axes has rotational vector \(\text{symmetry rep., } R_i\) (think about “orbiting about that axis”).
- Multiply symmetry rep. of ground state by \(R_i\).

\[
\begin{align*}
\text{SOC along } x(y) \text{ mixes } B_{1g} \text{ ground state with } E_g \text{ excited state (xz, yz)}
\end{align*}
\]

Result...

- \(D_{4h}\) symmetry Cu(II) complex.

\[
\begin{align*}
\therefore g\text{-values are anisotropic}
\end{align*}
\]

- Can predict that \(g_z > g_x = g_y \) (> \(g_e\))

- Exercise: \(x^2\) ground state for d9 (e.g. Jahn-Teller compressed CuII).
- Should find \(g_x > g_y > g_z\)

- Pattern of \(g\)-values tells you about the orbital in which the unpaired electron is located.
The magic pentagon

- Contributions to g-values summarised in…

\[ g = g_e - \frac{a^2 n \lambda}{\Delta E} \]

- Start at a vertex for a given ground state
- Links give contributions to \( g \)-values
- Coefficients \( n \) also given

How does this affect spectra?

- Fluid solution: field “sees” AVERAGE orientation

\[ g_{iso} = \frac{g_x + g_y + g_z}{3} \]

Single orientation spectra (e.g. single crystal)

- Each spectrum looks “isotropic”
- e.g. measure xz plane for our \( D_{4h} \) CuII example; \( g_z > g_x \)

- If we sum these, the “in-between” orientations cancel out

Powder spectra and “road maps”

- Powder spectrum is the SUM over ALL orientations
- Features observed at turning points in road map
- Different shapes and intensities due to summation

- Molecule has axial (disc-like) symmetry (\( D_{4h} \))
- Unique \( z \)
- Whole plane of xy
Powder spectra and symmetry

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Lecture V. Information about electronic structure

Information from g-values

Powder spectra with hyperfine: I = 1/2

- Pattern of g-values can identify SOMO
  - $d_{xy}$ or $d_{yz}$: $g_z > g_{x,y} > g_x$
  - $d_{z^2}$: $g_{x,y} > g_z = g_y$

- Each g-feature is split by hyperfine.
- Hyperfine coupling is also anisotropic, determined by symmetry.

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**Powder spectra: A vs. g-anisotropy**

- If \( A > \) separation between \( g \) in field units, then “parallel” and “perp” regions will overlap. Very common.
- E.g. typical \( \{VO\}^2^+ \): \( g_z = 1.93, \ g_{x,y} = 1.98, \ A_z = 170 \text{ G}, \ A_{x,y} = 60 \text{ G} \)

\[ H_0(g_x,y) - H_0(g_z) = 88 \text{ G} \]

\[ H_0(g_x,y) - H_0(g_z) = 880 \text{ G} \]

**More on hyperfine**

- **Fluid solution**: field “sees” AVERAGE orientation
- **Measure average A-value**, labelled \( A_{\text{iso}} \)

\[ A_{\text{iso}} = \frac{A_x + A_y + A_z}{3} \]

In energy \((\text{cm}^{-1})\) or frequency units \((\text{MHz})\) – NOT field units.

- \( A_{\text{iso}}, A_x, A_y \) and \( A_z \) can be either sign. No direct information in spectrum, BUT…
- Can get relative signs from averaging to \( A_{\text{iso}} \).
- Can also use \( A_{\text{iso}} \) to determine unresolved anisotropic component.

**Hyperfine Anisotropy**

Remember:
- Spin density **at nucleus**: \( A_i \)
- **SOC** \( = P\Delta g_{\text{iso}} \)
- **Dipolar**, \( A_{\text{dip}} \): Depends on e-n distance and orientation w.r.t. applied field.

- **In solid state, observe SUM of the isotropic and dipolar part.**
  \[ A = A_{\text{iso}} + A_{\text{dip}} \]

**Dipolar part of hyperfine**

\[ A_{\text{dip}} \propto \mu_{ez}\mu_{nz} \left( \frac{3\cos^2 \theta - 1}{r^3} \right) \]

- \( r = 0^\circ \quad 3\cos^2 \theta = +2 \)
- \( r = 90^\circ \quad 3\cos^2 \theta = -1 \)

Any dipolar interaction has form

+2\( a, -a, -a \)
Electron in a p<sub>z</sub>-orbital

Hyperfine observed for unit population of a p-orbital for that isotope. Calculated from theory.

\[
A_z = A_{iso} + \frac{4}{5} a^2 P_p
\]

\[
A_{x(y)} = A_{iso} - \frac{2}{5} a^2 P_p
\]

\[
A_z - A_{x(y)} = \frac{6}{5} a^2 P_p
\]

Angular factor from form of wavefunction

Exptly observed hyperfines

Covalency, \( a^2 \leq 1 \).

\( a = \) MO coefficient of p<sub>z</sub> in SOMO.

Anisotropic hyperfine \( \rightarrow \) composition of molecular orbitals!

Determining spin density distribution

\[
A_{iso}(P) = \pm 28 \text{ G} \rightarrow \pm 26 \times 10^{-4} \text{ cm}^{-1}
\]

\[
A_z(P) = \pm 118 \text{ G} \rightarrow \pm 110 \times 10^{-4} \text{ cm}^{-1}
\]

\[
A_{x,y}(P) = 15 \text{ G} \rightarrow 14 \times 10^{-4} \text{ cm}^{-1}
\]

Electron in a d<sub>xy/x^2-y^2</sub> orbital

Different angular factor for d-orbitals

SOC (excited state) contribution.

Convenient to cast in terms of g-shifts, because these can be measured.

Solve for \( a^2 \): spin density in d

Electron in a d<sub>2</sub> orbital

Example: covalency in Cu<sup>II</sup> complexes
**Example: covalency in CuII complexes**

Higher frequency (field) pulls g-values apart on field scale

- A$_{iso}$ = 76 x 10$^{-4}$ cm$^{-1}$
- g$_z$ = 2.260, g$_{x,y}$ = 2.050
- A$_z$ = 189 x 10$^{-4}$ cm$^{-1}$, A$_{x,y}$ = 20 x 10$^{-4}$ cm$^{-1}$

• A$_{iso}$, A$_z$, and A$_{x,y}$ all same sign (-ve)
• CFT predicts x$^2$-y$^2$ ground state
  \[ A_z - A_{x,y} = \frac{\Delta g}{7} \left[ -\frac{6}{7} a^2 + \Delta g_z - \frac{5}{14} \Delta g_{x,y} \right] \]
• $a^2$ = 0.77 for O-donor complex
• $a^2$ = 0.48 for S-donor complex
• Spin much more delocalised (i.e. greater covalency) for S-donor