Electron Paramagnetic Resonance: 
*Hyperfine Interactions*

Chem 634 
T. Hughbanks

What is EPR (ESR)?

- Electron Paramagnetic (Spin) Resonance
- Applies to atoms and molecules with one or more unpaired electrons
- An applied magnetic field induces Zeeman splittings in spin states, and energy is absorbed from radiation when the frequency meets the resonance condition, $h\nu = \Delta E \propto \mu_B \times H$
- $1/\lambda \sim 1 \text{ cm}^{-1}$, $\nu = c/\lambda \sim 10^{10} \text{ s}^{-1}$ (microwave, GHz)

Reading

- Drago’s *Physical Methods for Chemists* is still a good text for this section; it’s available by download (zipped, password protected): http://www.chem.tamu.edu/rgroup/dunbar/chem634.htm. For EPR: Chapters 9 and 13.
- Also good: *Inorganic Electronic Structure and Spectroscopy*, Vol. 1, Chapter 2 by Bencini and Gatteschi; and Vol. 2, Chapter 1 by Solomon and Hanson.
- Background references:
  - Orton, *Electron Paramagnetic Resonance*;
  - Abragam & Bleaney *Electron Paramagnetic Resonance of Transition Ions*;
  - Carrington & McLachlan, *Introduction to Magnetic Resonance*;

Spectroscopy: The Big Picture

<table>
<thead>
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<th>Spectral Range</th>
<th>EPR</th>
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<tbody>
<tr>
<td>γ-ray</td>
<td>X-ray</td>
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<tr>
<td>$&lt; 0.1 \AA$</td>
<td>5 Å</td>
</tr>
<tr>
<td>&gt; $10^5$</td>
<td>$2 \times 10^7$</td>
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<td>$2 \times 10^9$</td>
<td>$240 \times 10^9$</td>
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<td>$3 \times 10^{10}$</td>
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<th>Techniques</th>
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<th>NMR</th>
<th>NGR</th>
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Nuclear energies Chemical energies Molecular energies Spin energies
What information do we get from EPR?

- Chemists are mostly interested in two main pieces of information: **g-values** and **hyperfine couplings**, though spin-relaxation information can also be important to more advanced practitioners.
- **g-values**: these are, in general, the structure-dependent (i.e., direction-dependent) 'proportionality constants' that relate the electron spin resonance energy to the direction of the applied magnetic field: \( h\nu = g_{x,y,z} \mu_B H \). The direction-dependence is determined by electronic structure.
- **Hyperfine coupling**: arise from interactions between magnetic nuclei and the electron spin and give information about the delocalization of the unpaired electron.

What background do we need?

- We need an understanding of the magnetic properties of atoms and/or open-shell ions. In particular, we will need to understand the role of **spin-orbit coupling**, which is essential for understanding **g-value anisotropy**.
- Quantum mechanical tools: manipulation of **angular momentum operators** and understanding of how perturbation theory works.
- Basic ideas from MO theory and ligand field theory must be familiar.

Experimental Aspects

- EPR performed at fixed frequency (i.e., field is varied). Some common frequencies:
  - X-band: \( \nu \sim 9.5 \text{ GHz}, (9.5 \times 10^9 \text{ s}^{-1}; \lambda \sim 3 \text{ cm}) \); typical required field is ~ 3400 G = 0.34 T - most common \( (h\nu/g_e\mu_B = 3389.94 \text{ G for } \nu = 9.500 \text{ GHz}) \)
  - K-band: \( \nu \sim 24 \text{ GHz} \ (2.4 \times 10^{10} \text{ s}^{-1}; \lambda \sim 1 \text{ cm}) \); typical required field is ~ 8600 G = 0.86 T - less common \( (h\nu/g_e\mu_B = 8564.06 \text{ G for } \nu = 24.00 \text{ GHz}) \)
  - Q-band : \( \nu \sim 35 \text{ GHz} \ (3.5 \times 10^{10} \text{ s}^{-1}; \lambda \sim 0.8 \text{ cm}) \); typical required field is ~ 12500 G = 1.25 T \( (h\nu/g_e\mu_B = 12489.25 \text{ G for } \nu = 35.00 \text{ GHz}) \)
- Solvents: generally avoid water, alcohols, high dielectric constants (why?)

Experimental Aspects

- Form of samples:
  - Gases, liquids, solids, crystals, frozen solutions
  - Glasses are best for solution samples measured below solvent freezing points because they give homogeneity, whereas solutions have cracks and frozen crystallites and scatter radiation
- Note: glasses can form with pure solvents or mixtures. Unsymmetrical molecules have a greater tendency to form glasses. (e.g., cyclohexane crystallizes, methylcyclohexane tends to form glasses). H-bonding promotes crystallization.
Experimental Aspects

- Containers:
  - Pure silica ("quartz"), not Pyrex (borosilicate glass); the latter absorbs microwaves to too great an extent
- Constant, homogeneous magnetic fields.
- Microwave generator (klystron) - sets up a standing wave, for which the frequency is fixed by the geometry of the cavity.
- To improve the S/N ratio (reduce the effect of $1/f$ noise), the field is generally modulated (100-200 kHz) and detected with a lock-in detector (amplifier). Phase-sensitive detection gives a true differential of line shapes. For this reason, EPR spectra are normally displayed as derivatives – this is actually convenient since it accentuates features of the absorption in which we are interested anyway.

The Experiment

- EPR:
  - Fixed microwave frequency, sweep the field
  - In NMR, frequencies are varied at fixed fields
  - The power absorbed is measured as a function of field:
    $$P_{\text{microwave}}(H) \text{ at constant } v$$

H-atoms Spin Hamiltonian

- 1st term: electronic Zeeman
- 2nd term: nuclear Zeeman
- 3rd term: Fermi Contact hyperfine (isotropic) – magnitude depends on the electron density of the unpaired electron on the nucleus, $\psi(0)$.

* This is the "nuclear magneton" - a constant that is not 'nucleus specific' and is not the nuclear moment symbol used by Dragoe.

Electronic Zeeman interaction for H-atom

If a hydrogen atom is placed in a magnetic field, $\mathbf{H} = H_z \mathbf{\hat{z}}$, the electron's energy will depend on its $m_S$ value. The Zeeman interaction between the applied field and the magnetic moment of the electron is illustrated as:

$m_S = 1/2$

$$g_e \mu_B H$$

$m_S = -1/2$

$g_e = 2.002322...$
H-atom Spin Energies

Electronic Zeeman

Nuclear Zeeman

1st-order hyperfine
2nd-order hyperfine

Zero-field H-atom

\[ aS \cdot I = a(S I_x + S I_y + S I_z) = a\left(\frac{1}{2}(S I_x + S I_y) + S I_z\right) \]

\[ aS \cdot I | \alpha \alpha_x \rangle = a\left(\frac{1}{2}\right) | \alpha \alpha_x \rangle = \frac{1}{4} a | \alpha \alpha_x \rangle \]

\[ aS \cdot I | \alpha \beta_x \rangle = a\left(-\frac{1}{2}\right) | \beta \alpha_x \rangle = \frac{1}{4} a | \beta \alpha_x \rangle \]

\[ aS \cdot I \left[ \frac{1}{2} | \alpha \beta_x \rangle \pm | \beta \alpha_x \rangle \right] = a\left(\frac{1}{2}(S I_x + S I_y) + S I_z\right) \left[ \frac{1}{2} | \alpha \beta_x \rangle \pm | \beta \alpha_x \rangle \right] \]

\[ = \frac{1}{4} a \left[ | \alpha \beta_x \rangle \pm | \beta \alpha_x \rangle \right] + a\left(\frac{1}{4}\right) \left[ | \alpha \beta_x \rangle \pm | \beta \alpha_x \rangle \right] \]

\[ \pm a \left[ \frac{1}{2} \left( | \alpha \beta_x \rangle \pm | \beta \alpha_x \rangle \right) \right] - \frac{1}{4} a \left[ \frac{1}{2} \left( | \alpha \beta_x \rangle \pm | \beta \alpha_x \rangle \right) \right] \]

for +: \[ = \frac{1}{4} a \left[ \frac{1}{2} | \alpha \beta_x \rangle + | \beta \alpha_x \rangle \right] \]

for -: \[ = -\frac{3}{4} a \left[ \frac{1}{2} | \alpha \beta_x \rangle - | \beta \alpha_x \rangle \right] \]

Exact H-atom Spin Hamiltonian

from: Carrington & McLachlan, Introduction to Magnetic Resonance
most EPR measurements are

\[ \frac{1}{2}(|\alpha\alpha\rangle + |\beta\beta\rangle) \]

\[ \frac{1}{2}(|\alpha\beta\rangle + |\beta\alpha\rangle) \]

\[ \frac{1}{2}(|\alpha\beta\rangle - |\beta\alpha\rangle) \]

- A Note on units of energy
  - Three different units of energy (none of them really are energy!) are used in EPR:
    - \( \text{cm}^{-1} (1/\lambda) \), GHz or Hz or MHz (\( \nu \)), and gauss (G).
  - The conversions are done as follows:
    - \( \text{cm}^{-1} \times c \times 2.99793 \times 10^{10} \text{ cm/s} \rightarrow \text{Hz} \)
      or \( \text{cm}^{-1} \times 29.9793 \rightarrow \text{GHz} \)
    - \( \text{Hz} \times h / g \times H_B \times 3.5683 \times 10^{-7} \text{ G-s} \rightarrow \text{G} \)
      or \( \text{MHz} \times 0.35683 \rightarrow \text{G} \)
      or \( \text{cm}^{-1} \times 10697 \rightarrow \text{G} \)
  - The conversion to gauss yields the field necessary to induce an equivalent Zeeman splitting for a free electron.
  - Example: a zero field splitting parameter of 0.1012 cm\(^{-1}\) could also be reported as 3.034 GHz or 1082 G.
Methyl radical splitting diagram

• The four transitions for the methyl radical. 
  $+m_I$ states are lowest for $m_s = -1/2$ and the 
  $-m_I$ state lowest for $m_s = 1/2$, from the I-S term.

From Drago, “Physical Methods…” - Fig. 9-7 – corrected.

Methyl radical splitting diagram

• The four transitions for the methyl radical. 
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  $-m_I$ state lowest for $m_s = 1/2$, from the I-S term.

Plotted to reflect the constant-frequency experimental conditions.

Methyl radical Spectrum

• The four transitions for the methyl radical. 
  $+m_I$ states are lowest for $m_s = -1/2$ and the 
  $-m_I$ state lowest for $m_s = -1/2$, from the I-S term.

FIGURE 9-8 The derivative spectrum of the methyl radical in a CH$_4$ matrix at 4.2 K.

Organic $\pi$ Radicals

$\alpha_H = Q \rho_H ; \; Q = 22.5$ G
**ESR Spectrum: Naphthalide Anion**

- $a_\alpha = 13.79$ MHz ~ 4.92 G
- $a_\beta = 4.94$ MHz ~ 1.76 G

**Naphthalide Anion - SOMO**

- $B_{2g}$
- 0.429 (0.425)
- -0.258 (-0.263)

Numbers are coefficients from ESR (Hückel)

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**Table 1.1. Nuclear Moments and Spins**

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$I$</th>
<th>$g_\alpha$</th>
<th>$\gamma_\alpha$ (radians sec$^{-1}$ gauss$^{-1}$)</th>
<th>$Q$ (10$^{-28}$ cm$^3$)</th>
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<tr>
<td>H$^+$</td>
<td>1/2</td>
<td>5.585</td>
<td>26,753</td>
<td>0.00274</td>
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<tr>
<td>C$^{13}$</td>
<td>1/2</td>
<td>1.405</td>
<td>6,728</td>
<td>0.000355</td>
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<td>N$^{15}$</td>
<td>1/2</td>
<td>-0.567</td>
<td>-2,712</td>
<td>0.02</td>
</tr>
<tr>
<td>F$^{19}$</td>
<td>1/2</td>
<td>5.257</td>
<td>25,179</td>
<td>0.02</td>
</tr>
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<td>Si$^{29}$</td>
<td>3/2</td>
<td>-1.111</td>
<td>-5,319</td>
<td>0.0265</td>
</tr>
<tr>
<td>P$^{31}$</td>
<td>1/2</td>
<td>2.263</td>
<td>10,840</td>
<td>1.00 or -0.836*</td>
</tr>
<tr>
<td>Pt$^{185}$</td>
<td>1/2</td>
<td>1.120</td>
<td>5,747</td>
<td>0.3</td>
</tr>
<tr>
<td>S$^{34}$</td>
<td>3/2</td>
<td>0.429</td>
<td>2,054</td>
<td>0.064</td>
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<tr>
<td>Cl$^{35}$</td>
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<td>0.548</td>
<td>2,624</td>
<td>0.079</td>
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<tr>
<td>K$^{39}$</td>
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<td>0.261</td>
<td>1,250</td>
<td>0.113</td>
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<tr>
<td>V$^{37}$</td>
<td>7/2</td>
<td>1.468</td>
<td>7,033</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Nuclei with no spin: C$^{12}$ O$^{16}$ O$^{18}$ Si$^{28}$ S$^{32}$ Ca$^{40}$ *The quadrupole moment of Na$^{23}$ is uncertain.
Nuclei with I > $1/2$

- A nucleus with spin I splits the electron resonance into $2I + 1$ peaks.
- Again, the electronic Zeeman interaction is much larger than the hyperfine interaction.

\[ \text{Characteristic vanadyl EPR} \]
\[ g\text{-tensor is only modestly anisotropic (} g = 1.9658) \]

Nitronylnitroxide; Two $^{14}$N

For \( n \) identical nuclei, hyperfine splitting yields $2nI + 1$ lines.

\[ H_{\text{hyperfine}} = aS \cdot (I_1 + I_2) \]

\[ (I_1, I_2) \]

\[ \begin{array}{c}
(1,1) \\
(1,0) \\
(0,1) \\
(0,0) \\
(-1,0) \\
(-1,1)
\end{array} \]

\[ \begin{array}{c}
(1,1) \\
(1,0) \\
(0,0) \\
(-1,0) \\
(-1,1) \\
(-1,-1)
\end{array} \]

\[ \text{Delocalized Electrons in Clusters} \]

- $^{59}\text{Co}: 100\%$ abundance
- $I = 7/2$
- $2(3 \times 7/2) + 1 = 22$ expected lines

\[ \text{SOMO (a}_2\text{)} \]

\[ \text{Single crystal, 77K, H} \parallel z \]
Anisotropic hyperfine coupling

Simulated EPR spectrum of a normal copper complex, tetragonal Cu(H2O)6²⁺
(at X-band, \( n = 9.50 \) GHz). (A) EPR absorption; (B) first derivative spectrum without and (C) with copper hyperfine splitting.

\( ^{63}\text{Cu} \): 69.1% \( I = \frac{3}{2} \), \( A_0 = 4.95 \) GHz
\( ^{65}\text{Cu} \): 30.9% \( I = \frac{3}{2} \), \( A_0 = 5.30 \) GHz

Multiple hyperfine splittings


A gorgeous case of accidental degeneracy: 4 multiplets; each multiplet has 11 lines with relative intensity ratio:

1:2:3:4:5:6:5:4:3:2:1

Organic Radicals in Solids

\( H_{\text{Spin}} = g_e \mu_B H \cdot S - g_N \mu_N H \cdot I + S \cdot T \cdot I \)

- 1st term: electronic Zeeman (g-tensor anisotropy neglected)
- 2nd term (S⋅T⋅I): nuclear Zeeman
- 3rd term: Hyperfine – includes the isotropic Fermi contact term and the anisotropic, dipolar, part of the hyperfine (S⋅T′⋅I):

\[ S \cdot T \cdot I = S \cdot T' \cdot I + aS \cdot I \]
Dipolar Hyperfine Interaction

- The energy of dipole-dipole interactions falls off as the cube of the distance between dipoles - whether the dipoles are electric or magnetic.

\[
E_{\text{dipolar}} = \frac{1}{r^3} [\mathbf{\mu}_0 \cdot \mathbf{\mu}_1 - 3(\mathbf{\mu}_0 \cdot \mathbf{r})(\mathbf{\mu}_1 \cdot \mathbf{r})] \quad \mathbf{r} = \frac{\mathbf{r}}{|\mathbf{r}|}
\]

Hyperfine Anisotropy: \((\mathbf{S} \cdot \mathbf{T}') \cdot \mathbf{I}\) dominant over nuclear Zeeman, \(\mathbf{H} \cdot \mathbf{I}\)

If the dipolar hyperfine interaction dominated over the externally applied field (it often doesn’t), it would determine the axis of quantization of the nucleus. The hyperfine tensor determines the net angle between electron’s axis (along \(\mathbf{S}\)) and the nucleus’s axis, along \(\mathbf{S} \cdot \mathbf{T}'\).

Dipolar Hyperfine Interaction

- The electron is distributed over a volume defined by an orbital while the nucleus can be regarded as fixed at a point. Thus, the dipolar interaction is summed (integrated) over the electron’s probability distribution, \(|\psi|^2\).

The classical energy of interaction between two magnetic dipoles, \(\mathbf{\mu}_0\) and \(\mathbf{\mu}_1\), is

\[
E_{\text{dipolar}} = \frac{\mathbf{\mu}_0 \cdot \mathbf{\mu}_1 - 3(\mathbf{\mu}_0 \cdot \mathbf{r})(\mathbf{\mu}_1 \cdot \mathbf{r})}{r^3} \cdot \frac{1}{r^2}
\]

where \(r\) is the vector separating the dipoles.

The corresponding QM Hamiltonian is

\[
\mathbf{H}_{\text{dipolar}} = -\mu_0 \mu_1 \mathbf{S} \cdot \mathbf{r} \left| \frac{\mathbf{S} \cdot \mathbf{1} - 3(\mathbf{S} \cdot \mathbf{r})(\mathbf{I} \cdot \mathbf{r})}{r^3} \right|
\]

Dipolar Hyperfine: Origin of 2nd-order transitions

First-order EPR transitions we’ve seen involve the flipping of only the electron spin,

\[
|\alpha, \beta_i\rangle \leftrightarrow |\beta, \alpha_i\rangle \quad \text{and} \quad |\alpha, \beta_i\rangle \leftrightarrow |\beta, \alpha_i\rangle
\]

This is so because \(\langle \alpha_i | \beta_i \rangle = 0\) and \(\langle \alpha_i | \alpha_i \rangle = \langle \beta_i | \beta_i \rangle = 1\).

If the axis of quantization changes, both spins can flip

\[
|\alpha_i | \beta_i\rangle = \sin^2 \frac{\theta}{2} \quad \text{and} \quad |\alpha_i | \alpha_i\rangle = \cos^2 \frac{\theta}{2}
\]

Therefore, for some orientations, satellite transitions are observed. Detailed study yields signs of the tensor components.

When dipolar hyperfine interaction is comparable with the Zeeman field (a common case), it would determine the axis of quantization of the nucleus changes depending on whether electron is spin-up or spin-down. The hyperfine tensor determine the net angle between electron’s axis (along \(\mathbf{S}\)) and the nucleus’s axis, along \(\mathbf{S} \cdot \mathbf{T}'\).
The classical energy of interaction between two magnetic dipoles, \( \mathbf{\mu}_1 \) and \( \mathbf{\mu}_2 \), is
\[
E_{\text{dipolar}} = -\frac{\mathbf{\mu}_1 \cdot \mathbf{\mu}_2}{r^3} - \frac{3(\mathbf{\mu}_1 \cdot \mathbf{r})(\mathbf{\mu}_2 \cdot \mathbf{r})}{r^5} - \frac{1}{r^3}
\]
where \( \mathbf{r} \) is the vector separating the dipoles.

The corresponding QM Hamiltonian is
\[
\mathbf{H}_{\text{dipolar}} = -\frac{\mathbf{\mu}_1 \cdot \mathbf{\mu}_2}{r^3} - \frac{3(\mathbf{\mu}_1 \cdot \mathbf{r})(\mathbf{\mu}_2 \cdot \mathbf{r})}{r^5} - \frac{1}{r^3}
\]

• Matrix elements of \( \mathbf{T}' \) should be interpreted as expectation values of the operators shown over the electronic wavefunction. (The origin is at the nucleus at which the spin \( \mathbf{I} \) resides.)

\[
\mathbf{T}' = \mathbf{T} + \alpha \mathbf{I}
\]

Hyperfine Anisotropy

Example: Malonate Radical

• The malonate radical is obtained by irradiation of malonic acid with x-rays. The trapped radical can be studied with single-crystal EPR - which reveals the anisotropy of the hyperfine tensor, \( \mathbf{T}' \). (We can initially ignore the Zeeman interaction of the proton, \( \mathbf{H} \cdot \mathbf{I} \), i.e., consider only the first-order effects resides.)

Hyperfine Anisotropy; Example: [VO(CN)\textsubscript{5}]\textsuperscript{3–}

- The EPR spectrum of the [VO(CN)\textsubscript{5}]\textsuperscript{3–} ion in a single crystal of KBr is shown above; the magnetic field is aligned along the [100] axis of the KBr host.

a) What are the values of $A_{||}$ and $A_{\perp}$? *(Hint: There are two overlapping spectra shown here. Think about the way in which the [VO(CN)\textsubscript{5}]\textsuperscript{3–} ion is likely to substitute for K\textsuperscript{+} and Br\textsuperscript{–} ions in the host; the relative intensities of the two spectra should settle which spectrum corresponds to the $||$ direction and which corresponds to the $\perp$ direction.)*

[b] Explain the relative magnitudes of the hyperfine constants.

c) Identify all the lines in the spectrum. $g_{||} = 1.9711$; what is the value of $g_{\perp}$?

d) Draw a $d$-orbital splitting diagram for this ion ($\pi$-effects are important too) and use the $g$-value information to determine as many of the $d$-orbital energy splittings as you can from the information you have so far (for V\textsuperscript{4+}, $\zeta = 248$ cm\textsuperscript{–1}) assuming the orbitals have pure $d$-character.

e) Consider the effects of covalence in the calculation of the $g$-values for this ion and discuss how the important ligand bonding effects should influence both $g_{||}$ and $g_{\perp}$. 

See Wertz & Bolton, p. 320.