Isotropic EPR spectra of s = ½ paramagnets
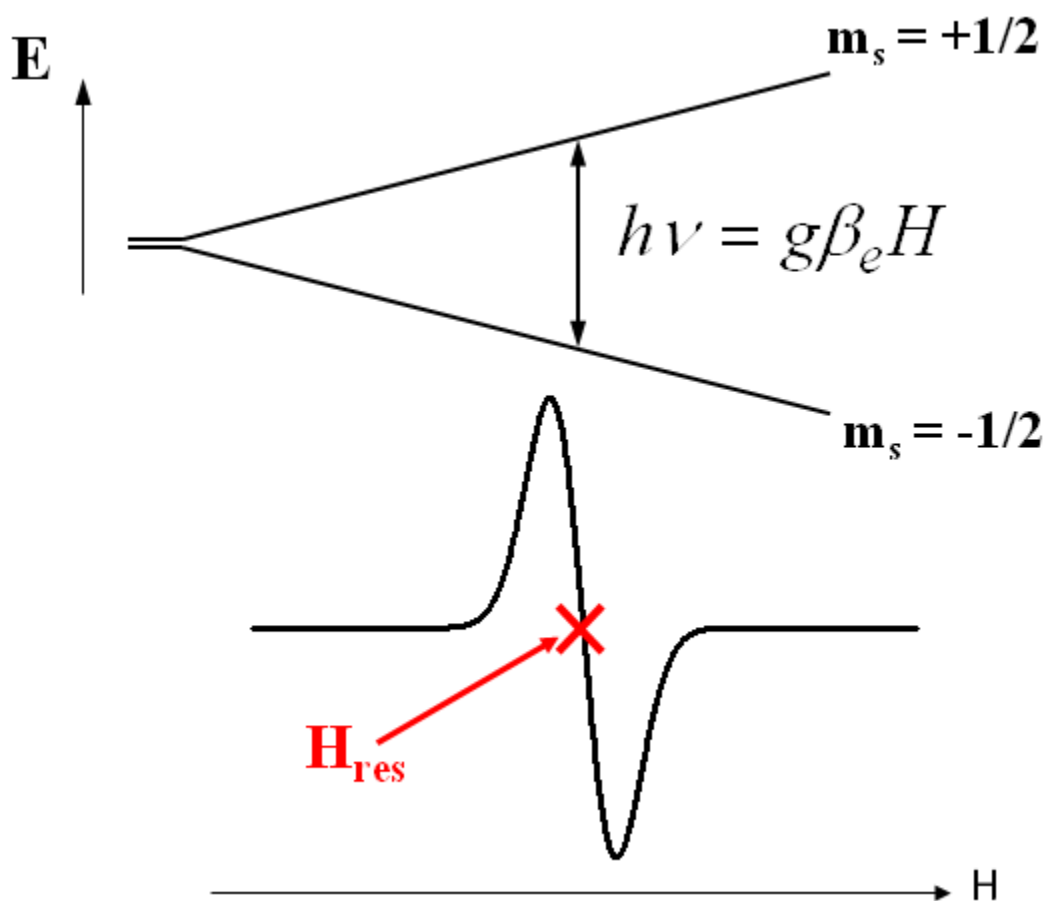
(i)   Resonance and the g-value

An electron has an intrinsic spin (s = ½) and an associated magnetic moment. Hence, it will interact with an applied magnetic field in an analogous fashion to nuclear spins in NMR spectroscopy. This is called the Zeeman effect.

Zeeman effect in EPR

The Zeeman splitting is given by:

$$\Delta E = g\beta H$$

where β is the Bohr magneton (a fundamental constant) and H is the applied magnetic field strength. The electronic g-value (or g-factor) of a free electron is a dimensionless fundamental constant, g_e = 2.002316. Spin flips with the selection rule Δm_s = ±1 can be induced by electromagnetic radiation of frequency υ such that:

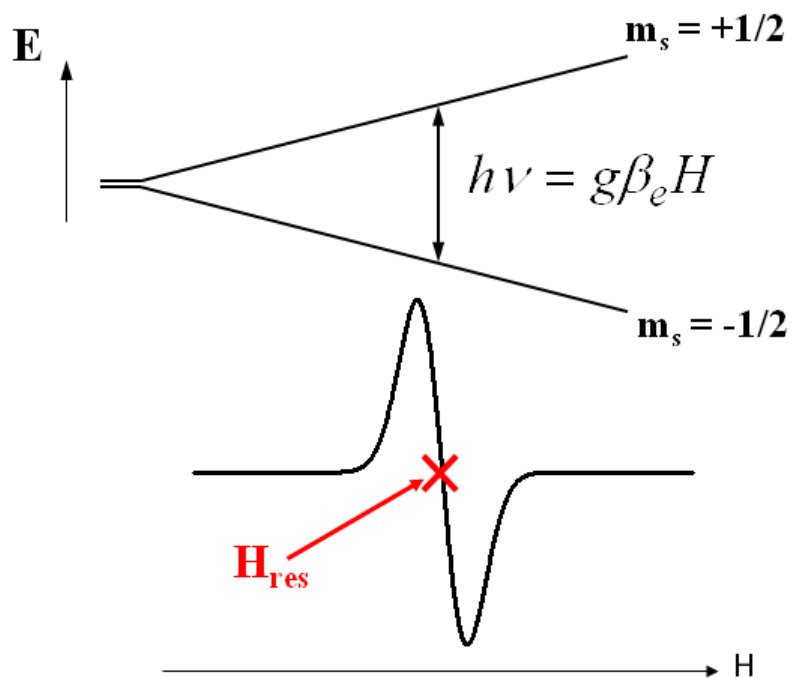$h\upsilon = g\beta H$

This is an EPR transition. It is more convenient experimentally to hold a static microwave frequency, and sweep the magnetic field. The signal is detected as the first harmonic, hence derivative lineshapes are usually presented (as above).

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where β is the Bohr magneton (a fundamental constant) and H is the applied magnetic field strength. The electronic g-value (or g-factor) of a free electron is a dimensionless fundamental constant, ge = 2.002316. Spin flips with the selection rule $\Delta m_s = \pm 1$ can be induced by electromagnetic radiation of frequency υ such that:

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For real samples, the g-value deviates from ge (because of a contribution to the magnetic moment from orbital angular momentum), and is an experimental observable which is a characteristic of the paramagnet. The deviation of the g-value from ge depends on the nature of the orbital containing the unpaired electron, the energy of nearby filled or vacant orbitals, and the magnitude of spin-orbit coupling. Hence, g-values for free-radicals are close to 2.0 while those for transition ions can vary widely.

The electron magnetic moment is much bigger than the nuclear magnetic moment (because of its much lighter mass), hence smaller magnetic fields and higher frequencies (typically microwaves) are necessary for EPR. The large magnetic moment makes EPR very sensitive and also makes the influence of the electron felt to much longer distances than nuclear spin (this is exploited in several areas of application). The price that is paid is the much shorter relaxation times, giving rise to larger linewidths (typically MHz) and making pulsed spectroscopy more challenging than in NMR.

The table below lists commonly used (commercially available) microwave frequencies, and the magnetic fields necessary to achieve resonance for g = 2.000. Frequencies up to Q-band can be performed using an electromagnet, while W-band and higher frequencies require a superconducting magnet. EPR is now performed up to THz frequencies in several laboratories.

Microwave Band	Frequency (GHz)	B_{res}(Gauss)
L	1.1	392
S	3.0	1070
X	9.75	3480
K	24.0	5870
Q	34.0	12100
W	94.0	33600

(ii)   Hyperfine splitting

The electron spin can interact with non-zero nuclear spins (I > 0) – this is called the hyperfine interaction (or coupling). For a single nuclear spin I = ½, this now gives two allowed EPR transitions:
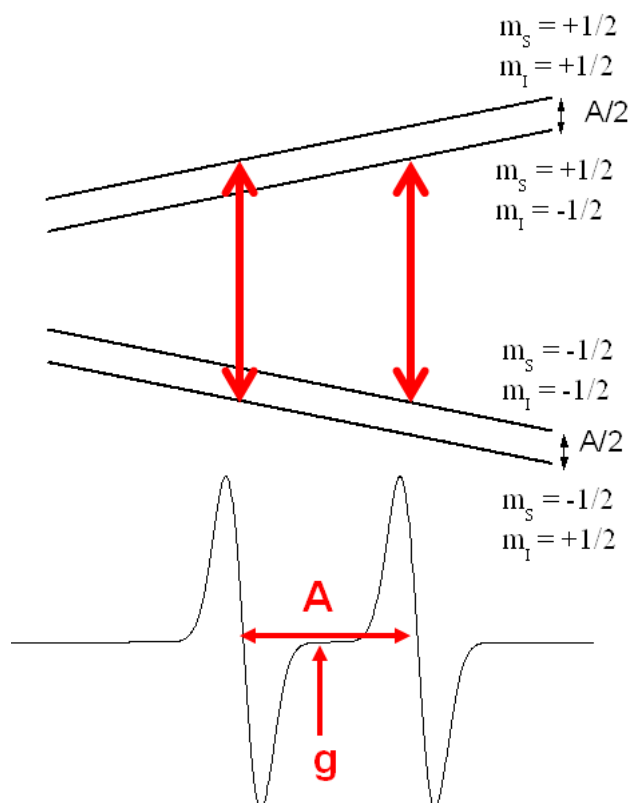
The additional selection rule is DmI = 0 ("flip the electron spin, leave the nuclear spin alone"), giving rise to 2nI+1 transitions where n is the number of equivalent nuclei of spin I. The relative intensities are given by a Pascal's triangle, in direct analogy to multiplet splittings in NMR. A triangle for I = ½ is shown below and is generated by adding up 2I + 1 (= 2) numbers to obtain the entries in the next row.

n					0		1		0					#	Σ
1				0		1		1		0				2	2
2			0		1		2		1		0			3	4
3			1		3		3		1					4	8
4		1		4		6		4		1				5	16
5	1		5		10		10		5		1			6	32
6	1		6		15		20		15		6		1	7	64
7	1		7		21		35		35		21		7	1	8	128
8	1	8		28		56		70		56		28	8	1	9	256

In contrast to NMR spectroscopy, it is often easy to observe couplings of the electron spin to quadrupolar nuclei, i.e. nuclei with I > ½. The relative intensities in the multiplet can be determined by a binomial triangle, in which succeeding rows are again generated by adding up 2I + 1 numbers, as shown below for I = 1.
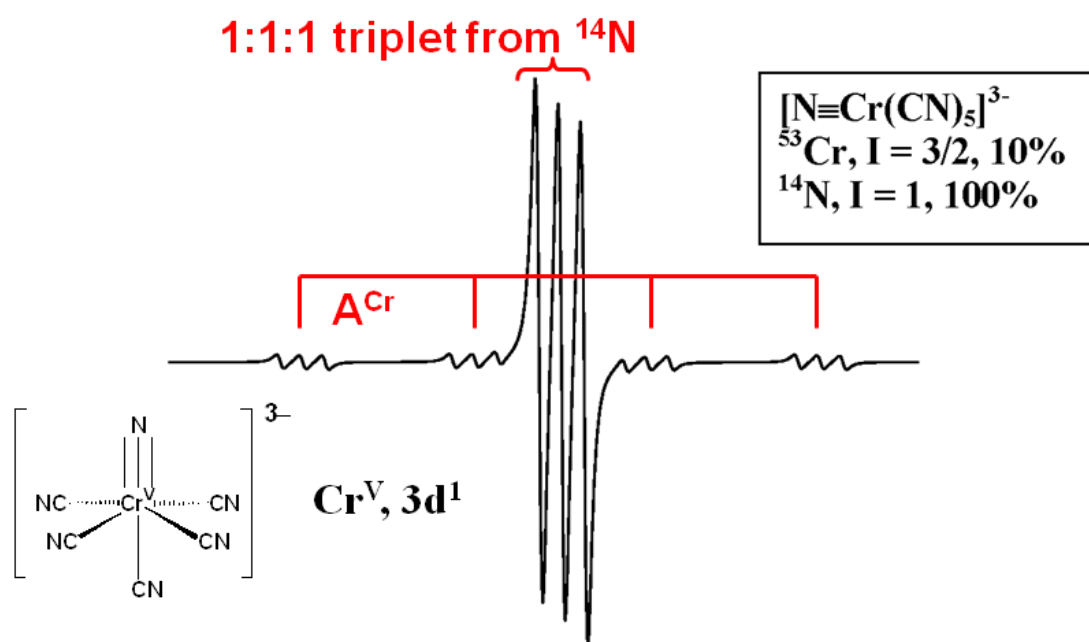
n														#	Σ
n					0	0	1	0	0						
1				0	0	1	1	1	0	0				3	3
2			0	0	1	2	3	2	1	0	0			5	9
3			0	1	3	6	7	6	3	1				7	27
4			1	4	10	16	19	16	10	4	1			9	81
5		1	5	15	30	45	51	45	30	15	5	1		11	243
6	1	6	21	50	90	126	141	126	90	50	21	6	1	13	729

For both of these triangles the number of lines (#) is given by $(2 \times n \times I) + 1$, where n is the number of equivalent nuclei of spin I. The sum (Σ) across a given row is given by $(2 \times I + 1)n$, which allows the construction of any triangle to be checked.

Many elements are multi-isotopic in natural abundance, and each isotope will give rise to a characteristic spectrum, exactly analogous to e.g. 13C satellites in NMR.

Hyperfine coupling patterns can be used to identify radicals, because the observed multiplet patterns reveal the nuclear spins present. Moreover, because electrons are mobile (cf. nuclei), hyperfine structure also gives detailed information on the electronic structure of the paramagnet (e.g. the nature of the singly occupied orbital). The magnitudes of the coupling constants depend on the strength of interaction between the electron and the nucleus. This can arise from the dipolar interaction, or from unpaired electron density at the nucleus. Dipolar interactions average to zero in fluid solution (i.e. averaged over all orientations), hence hyperfine coupling in fluid solution must arise from spin density at the nucleus. This can arise from direct s-orbital electron spin density (p, d and f-orbitals having nodes at the nucleus) or indirectly via spin polarisation (this is why organic p-radicals give rich proton hyperfine structure despite the 1H nuclei lying in the planar node).

Many of these effects are illustrated in the example below, of a chromium(V) nitrido complex, [Cr(N)(CN)5]3-:

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

$[N{\equiv}Cr(CN)_5]^{3-}$
$^{53}Cr, I = 3/2, 10\%$
$^{14}N, I = 1, 100\%$

A^{Cr}

$Cr^V, 3d^1$

Chromium [CrV is d1, hence the complex is paramagnetic] has one non-zero nuclear spin isotope; 53Cr has I = 3/2 and a natural abundance of 9.5%. Hence, for 9.5% of molecules in the sample the unpaired electron couples with an I = 3/2 nucleus giving a 1:1:1:1 quartet. The remaining 91.5% of molecules have no nuclear spin on Cr, and these give a singlet. 14N (99.6% natural abundance) has I = 1, and this gives rise to the 1:1:1 triplet structure of each multiplet (this arises from the single nitrido ligand rather than the cyanides). The term "superhyperfine" coupling is often used to describe hyperfine to ligand nuclei in transition metal compounds, because this splitting is usually (but not always) smaller than that from the metal isotopes.

Hyperfine coupling constants are usually measured in magnetic field units, i.e. G or mT, but should really be converted into energy or frequency units. This conversion depends on the associated g-value. For example, for g = 2.00 and a measured A = 100 G, then from DE = hν = gβHr (β = 4.66858 x 10-5 cm-1 G-1):

A(cm-1) = g × β × A(G)= 2.00 × 4.66858 × 10-5× 100= 93.4 × 10-4 cm-1 A(MHz) = g × A(G) / 0.7145= 2.00 × 100 / 0.7145= 280 MHz

(iii) Motional effects

Spectra measured from fluid solutions often display linewidths which vary from transition to transition. For example, the spectrum below is of [VO(acac)2] (Hacac = acetylactetone). The single unpaired electron (VIV, d1) interacts with the 51V nucleus (I = 7/2, 99.8% natural abundance) giving a 1:1:1:1:1:1:1:1 octet. The amplitudes of the lines vary across the octet, as do the linewidths: the intensity (double integral) of each transition is the same. The variable linewidth is caused by a tumbling rate of the molecule in solution which is comparable to the microwave frequency of the experiment and consequent incomplete orientation averaging of the spectrum (see Primer Part II). Such effects can be modelled to give information on the motion of radicals; this is often exploited with e.g. nitroxide spin probes in biological materials to study relative mobility at selected sites.