What is EPR ?

Electron Paramagnetic Resonance

a.k.a. ESR

Electron Spin Resonance

a.k.a. FMR

Ferro Magnetic Resonance

Proposed topics

-1- EPR fundamentals for an isotropic S=1/2 system,

-2- anisotropy and hyperfine effects on S=1/2,

-3- biradicals and effects of spin-orbit coupling,

-4- a qualitative fly-over of transition metal ions.

Today's goals

Origin of the signals: magnetic moments, introduction to g and β_e
Practical aspect #1: field-swept instead of frequency swept.
g: a wee bit o' cool physics
Practical aspect #2: consequences of the size of β_e
Practical aspect #3: signals are reported in terms of g
Practical aspect #4: signals are detected in derivative form

Origin of EPR signals, w. comparisons to NMR signals

Observe unpaired electrons. These are often the agents of important chemistry.

Interaction between electron magnetic moment and magnetic field produces energy levels. (Similar to NMR)

A fixed frequency is used to collect data as a function of a swept magnetic field. (Different from NMR)

A more favourable Boltzmann population offsets the generally lower concentrations of unpaired electrons.

Information in the g-value.

Chemical species with unpaired electrons

Free radicals in gases, liquids or solids.

Some point defects in solids (eg. upon γ irradiation).

Biradicals (molecules containing two unpaired electrons remote or otherwise very weakly interacting with one-another).

Triplet ground or excited states (two unpaired electrons that interact strongly).

More unpaired electrons.

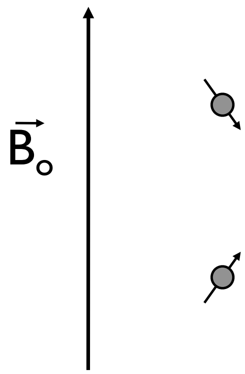
Transition metal ions and rare-earth ions.

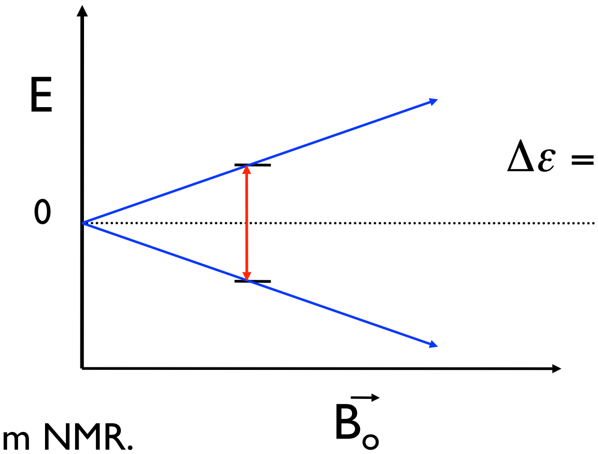
More common than perceived, readily detectable and richly informative.

Like NMR, alignment and energies in a magnetic field: $\vec{\mu} \bullet \vec{B}$

$$\varepsilon = -\overrightarrow{\mu_I} \bullet \vec{B} \qquad \mu_I = \gamma \hbar m_I = \beta_N m_I \qquad \varepsilon = -\gamma \hbar m_I B_o = \mp \hbar \gamma B_o / 2$$

$$\Delta\varepsilon = h\nu = \hbar\gamma B_o$$





$$\Delta\varepsilon = \hbar\gamma B_o$$

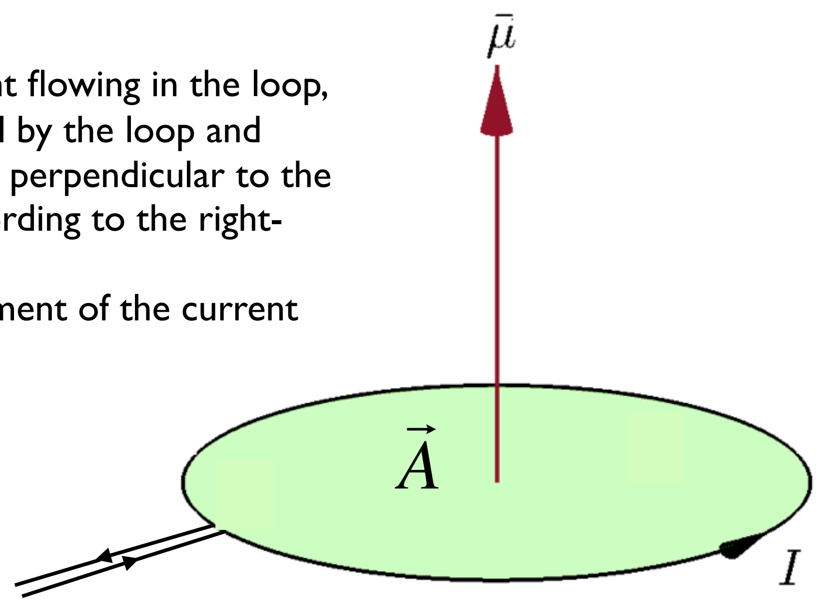
But presentation is different from NMR.
In part because μ_e is not as simple as μ_I.

Magnetic moment of an electron: a classical current loop.

$$\vec{\mu} = I\vec{A}$$

I is the electric current flowing in the loop,
A is the area enclosed by the loop and
vector A has direction perpendicular to the plane of the loop according to the right-hand rule.
μ is the magnetic moment of the current loop.

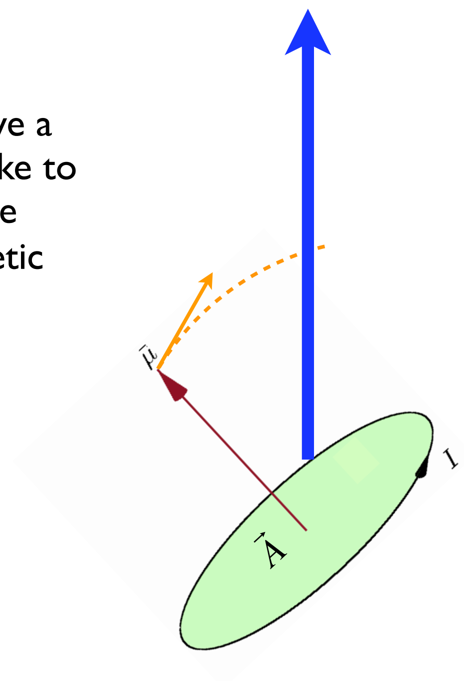
Units of μ are A m^2



http://en.wikipedia.org/wiki/File:LoopCurrentMagneticMoment.png

$$\vec{\mu} = I\vec{A}$$

The current loop is considered to have a magnetic moment because it would like to rotate in a magnetic field such that the vector μ precesses around the magnetic field.



$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

τ is the torque and B is the magnetic field.

Units for Torque are Nm = |μ| T making the units of μ Nm/T or J/T.

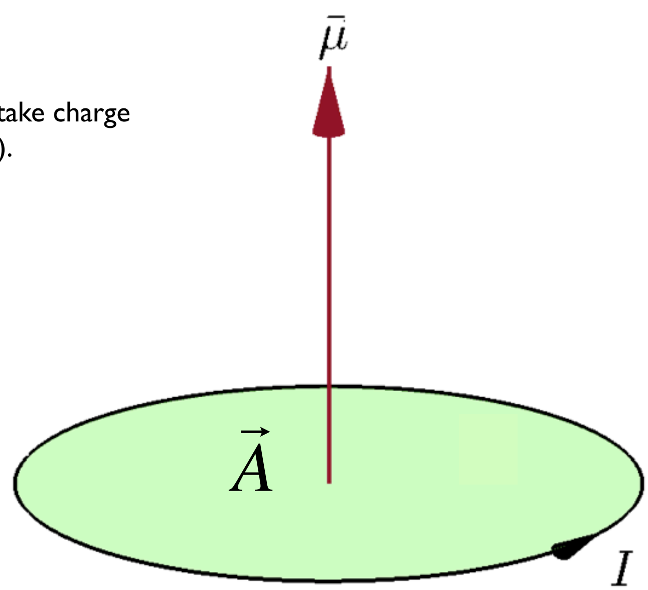
$$\vec{\mu} = I\vec{A}$$

$$A = \pi r^2 \qquad I = \frac{qv}{2\pi rc}$$

The factor of c (speed of light) is needed to take charge in C to electromagnetic Gauss units ($c=\mu_o\varepsilon_o$).

$$\vec{\mu} = \frac{qmvr}{2mc} = \frac{q}{2mc} m_l \hbar$$

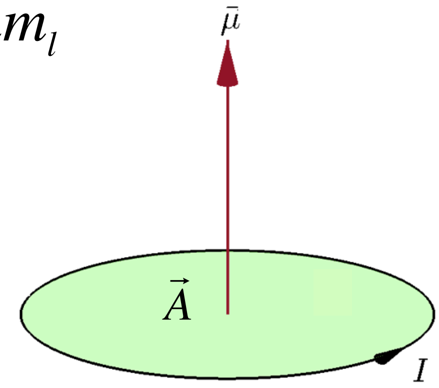
for **pure orbital angular momentum** (no spin).



(Recall: mv=p (momentum), mvr=L (angular momentum))

http://en.wikipedia.org/wiki/File:LoopCurrentMagneticMoment.png

$$\vec{\mu} = \frac{q}{2mc} m_l \hbar = \frac{-e}{2mc} m_l \hbar = \gamma \hbar m_l$$



$\frac{q}{2mc} = \gamma$ for **pure orbital angular momentum.**

$\frac{-ge}{2mc} = \gamma$ for **electrons, with spin.**

Make g explicit: isolate from other parameters

g'll be back

$$\vec{\mu} = \frac{-ge}{2mc} m_l \hbar = -g \beta_e m_l$$

$\beta_e = \frac{e\hbar}{2mc}$ is the Bohr magneton, also denoted by μ_B.

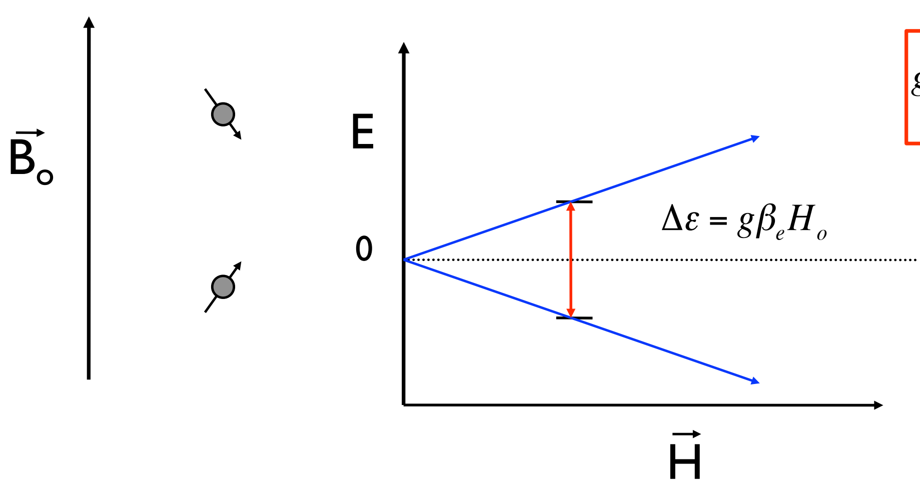
Alignment and energies in a magnetic field: $\vec{\mu} \parallel \vec{H}$

$$\varepsilon = -\vec{\mu} \bullet \vec{B}$$

$$\varepsilon = g\beta_e m_I B_o = \pm g\beta_e B_o / 2$$

$$\Delta\varepsilon = h\nu = g\beta_e H_o \qquad H_{res} = \frac{h\nu_o}{g\beta_e}$$

$$\boxed{g = \frac{h\nu_o}{\beta_e} \frac{1}{H_{res}}}$$



EPR uses a fixed frequency ν and spectra are displayed vs. variable H.
NMR uses a fixed field H and spectra are displayed vs. ν (scaled as $(\nu-\nu_o)/\nu_o$).

Choices of fixed frequency for EPR

340 mT

X-band: B_o = 3400 Gauss, ν_o = 9.5 GHz

B_o = 3300 Gauss, ν_o = 9.2 GHz

K-band: B_o = 8600 Gauss, ν_o = 24 GHz

Q-band: B_o = 1.25 T, ν_o = 35 GHz

L-band: B_o = 300 Gauss, ν_o = 1 GHz

S-band: B_o =1100 Gauss, ν_o = 3 GHz

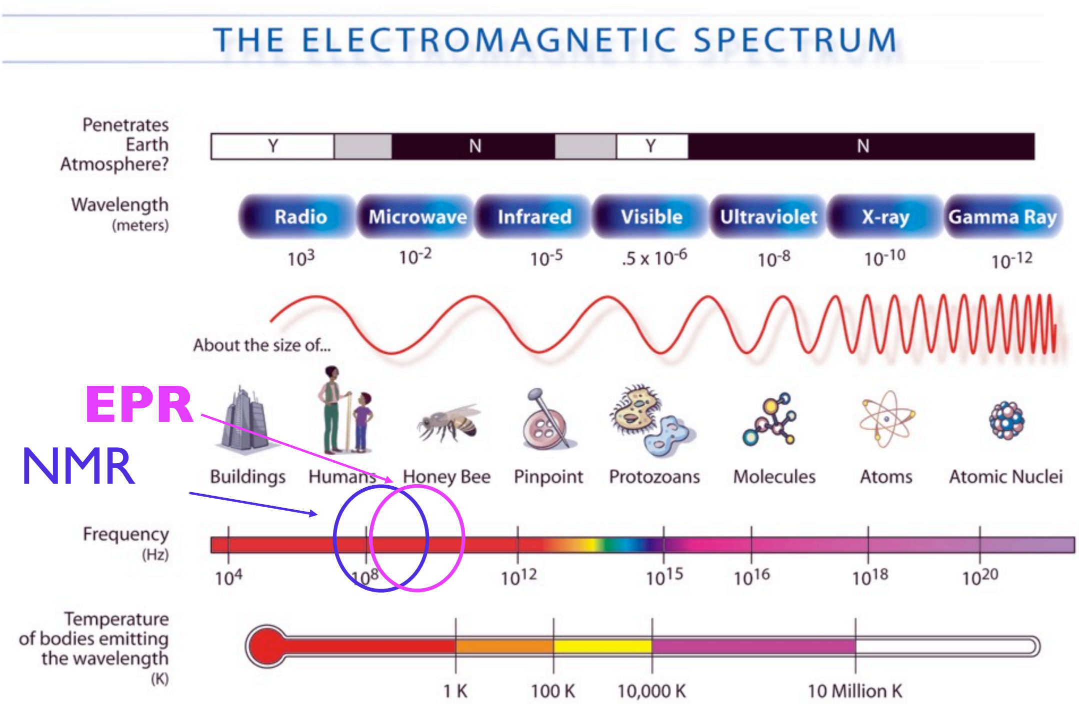
W-band: B_o = 3.5 Tesla, ν_o = 95 GHz

(1 Tesla = 10^4 Gauss)

Waveband	L	S	C	X	P	K	Q	U	V	E	W	F	D	—	J	—
λ / mm	300	100	75	30	20	12.5	8.5	6	4.6	4	3.2	2.7	2.1	1.6	1.1	0.83
ν / GHz	1	3	4	10	15	24	35	50	65	75	95	111	140	190	285	360
B_0 / T	0.03	0.11	0.14	0.33	0.54	0.86	1.25	1.8	2.3	2.7	3.5	3.9	4.9	6.8	10.2	12.8

Sunney Chan, then at Caltech

EPR in the EM spectrum



http://en.wikipedia.org/wiki/electromagnetic-spectrum

Review: The small size of the NMR quantum

4×10^8 Hz is a very low frequency,
corresponding to a low energy for the quantum transition.

X-band EPR is conducted at 9.5 GHz = 9.5×10^9 Hz, 20 x higher.

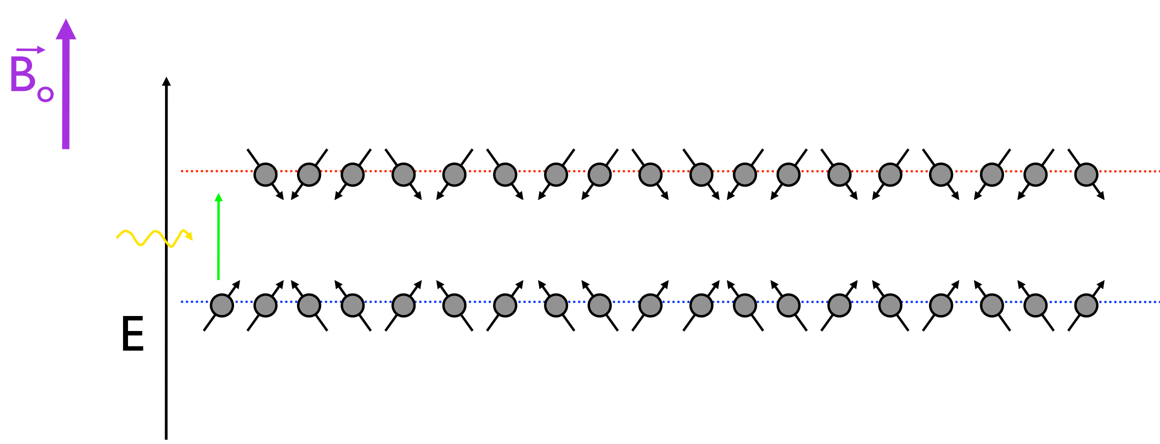
eg. optical transitions, eg at 500 nm (cytochromes are at 550 nm)
$\nu = c/\lambda = 3 \times 10^8\ \mathrm{m\ s^{-1}} / 550 \times 10^{-9}\ \mathrm{m} = 5.5 \times 10^{14}\ \mathrm{s^{-1}}$
$= 5.5 \times 10^{14}$ Hz, 10^6 times higher.

On the positive: NMR is a non-perturbative method: irradiation does not cause change, break bonds.

On the negative, the signals are very weak, for TWO major reasons: Boltzmann population excess is small and Einstein spontaneous recovery rate is slow.

Boltzmann consequences of the small quantum

Only a very small excess of the population is in the ground state, only this small fraction supports NET absorption of radiation.



NMR Consequences of Boltzmann

$\mathbf{P_{exc}/P_{ground} = e^{-(\Delta E/kT)}}$ $\Delta E/kT = h\nu/kT$

$\Delta E/kT = 6.6\times10^{-34} \cdot 4\times10^{8} J/1.4\times10^{-23} \cdot 300K = 6.3\times10^{-5}$
$\mathbf{P_{exc}/P_{ground}} = e^{-.000063} = .99994$

$P_{ground}/P_{total} = 1/(1.99994) = .500\,016 = .500\,00 + .000\,016$

Only 0.000 016 x the concentration of the sample actually produces signal.

1 M Samples contain ≈ 15 μM signal-producing molecules, net.

EPR Consequences of Boltzmann,

at the same magnetic field

$g\beta_e$ is 660 x $\gamma\hbar$

$\Delta E/kT = 660\times6.3\times10^{-5} = .042$
$\mathbf{P_{exc}/P_{ground}} = e^{-.042} = .959$

$P_{ground}/P_{total} = 1/(1.959) = .51$

Now 0.01 x the concentration of the sample produces signal.
(vs. 0.000 016 x)

1 M Samples contain ≈ 10 mM signal-producing molecules, net.
(vs. 15 μM)

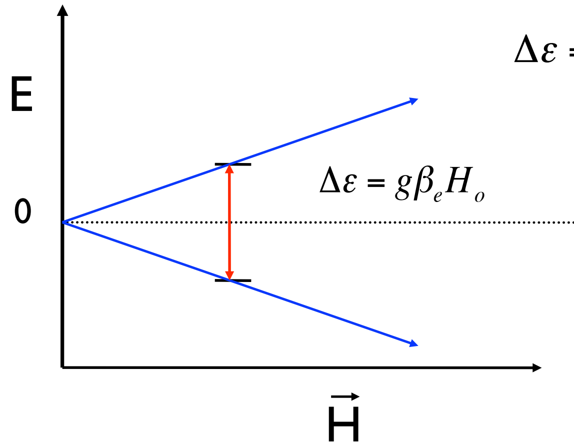
We need not use such high fields
and/or we need not use so much sample.

Information content in g

$$\varepsilon = -\vec{\mu} \bullet \vec{B}$$

$$\varepsilon = g\beta_e m_I B_o = \pm g\beta_e B_o / 2$$

$$\Delta\varepsilon = h\nu = g\beta_e H_o$$



$$\boxed{g = \frac{h\nu_o}{\beta_e}\frac{1}{H_{res}}}$$

For a free electron,
g_e = 2.00232

In EPR spectra g can range from **10 to 1** (and beyond).

5-fold variations vs. ppm variations observed in NMR.

Range reflects orbital contributions, spin multiplicity and spin-spin coupling.

Free electron g_e = 2.00232

Angular momentum due only to spin.

Value close to 2 (as opposed to 1 for purely orbital angular momentum): relativistic effects at work.

Deviation from exactly 2.000 : QCD corrections.

For Later: when orbital angular momentum becomes significant in addition to spin, we will need to consider total angular momentum J.
J=S + L
g_J is the Landé g-factor. This is used for transition metal ions in lower rows.

When orbital effects are relatively small, we can treat them most simply as a perturbation and account for them in a tensor g based on g_e.

http://en.wikipedia.org/wiki/G-factor_%28physics%29
http://en.wikipedia.org/wiki/Land%C3%A9_g-factor

Free electron g_e = 2.00232

Value close to 2 (as opposed to 1): relativistic effects at work.

Deviation from exactly 2: QCD corrections.

$$\vec{\mu} = \frac{q}{2mc} m_l \hbar = \frac{-e}{2mc} m_l \hbar = \gamma \vec{L}$$

γ is the gyromagnetic ratio (= magnetogyric ratio)

$\frac{q}{2mc} = \gamma$ **pure orbital angular momentum** g_L = 1. (from pg. 9)

$\frac{-ge}{2mc} = \gamma$ **electrons, g_s ≈ 2** because electrons are **relativistic particles,** especially near the nucleus.

At relativistic speeds, $E^2 = p^2c^2 + m^2c^4$ holds. Dirac showed that this requires consideration of positrons associated with electrons. Whereas the Schödinger equation is based on two components $\varphi_\uparrow$ and $\varphi_\downarrow$, the additional $\overline{\varphi}_\uparrow$ and $\overline{\varphi}_\downarrow$ of Dirac also contribute to $\vec{\mu}$, **doubling the charge carriers and thus γ**.

Free electron g_e = 2.00232

Value close to 2 (as opposed to 1): relativistic effects at work.

Deviation from exactly 2: QCD corrections.

Quantum Chromodynamics corrections. higher-order terms reflecting interactions between positrons and electrons produce the correction of + 0.002319

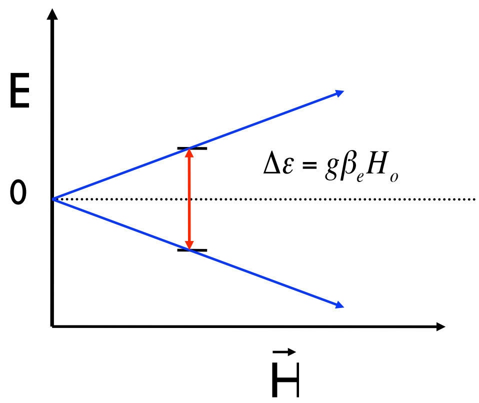
(g-2)/2 = a = 0.00115965218111 ± 0.00000000000074 (1 part in 10^9)

g has been measured to an accuracy of 1 part in 10^{12}.

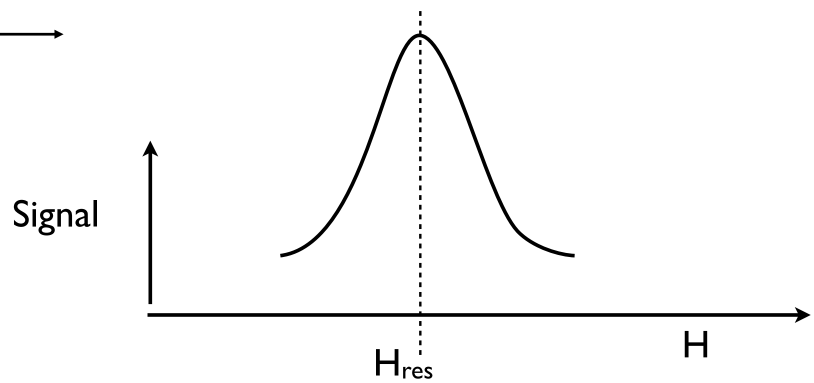
http://en.wikipedia.org/wiki/Dirac_equation
http://en.wikipedia.org/wiki/G-factor_%28physics%29
http://en.wikipedia.org/wiki/Anomalous_magnetic_dipole_moment

Implications for the observed spectrum

From pg. 10



$$H_{res} = \frac{h\nu_o}{g\beta_e}$$



Implications for the observed spectrum

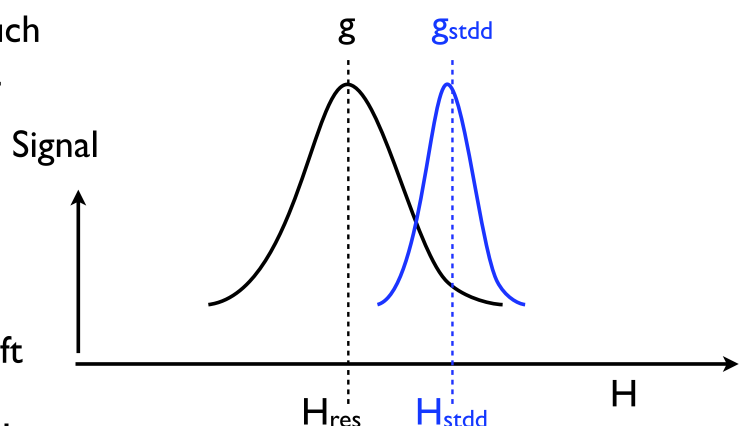
From pg. 10

$$H_{res} = \frac{h\nu_o}{g\beta_e} \qquad gH = \frac{h\nu_o}{\beta_e}$$

known g-value standard such as dpph g=2.0037 ±0.0002

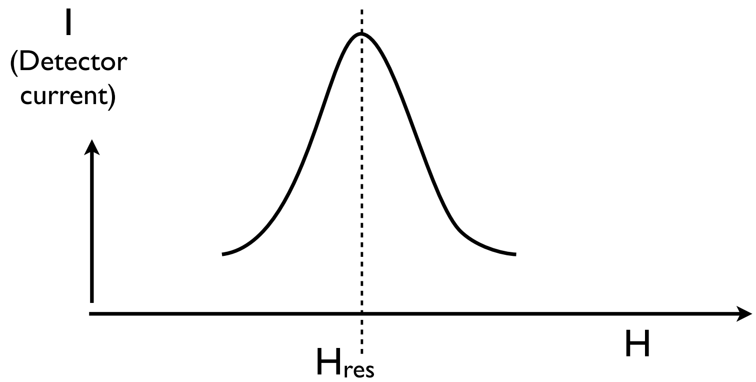
$$g_x = \frac{g_{stdd} H_{stdd}}{H_x}$$

Logic similar to chemical shift referencing.
Retain $(H_x - H_{stdd})/H_{stdd} < 0.01$



Field modulation with lock-in amplifier

Add to the swept field a small additional field oscillating at 100 kHz. Noise will fluctuate at random frequencies but the signal is now identified as that which fluctuates at 100 kHz. Only frequencies within 1 Hz of 1 kHz are collected.



Field modulation with lock-in amplifier

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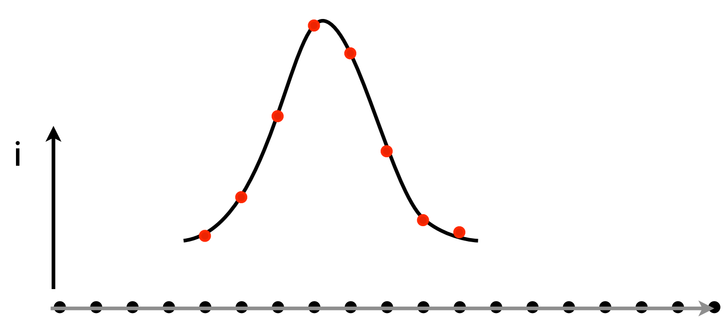
Photo of cavity,



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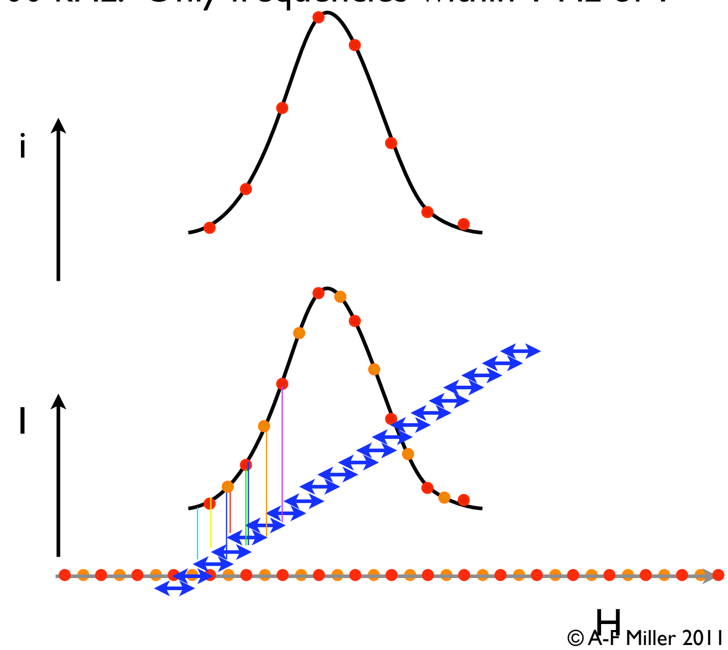
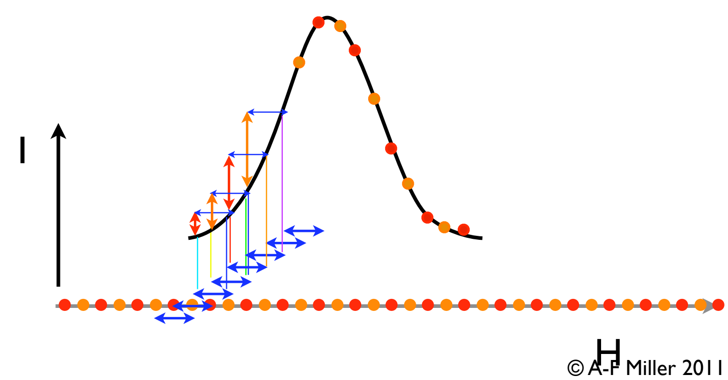


Field modulation with lock-in amplifier

Add to the swept field a small additional field oscillating at 100 kHz. Noise will fluctuate at random frequencies but the signal is now identified as that which fluctuates at 100 kHz. Only frequencies within 1 Hz of 1 kHz are collected.

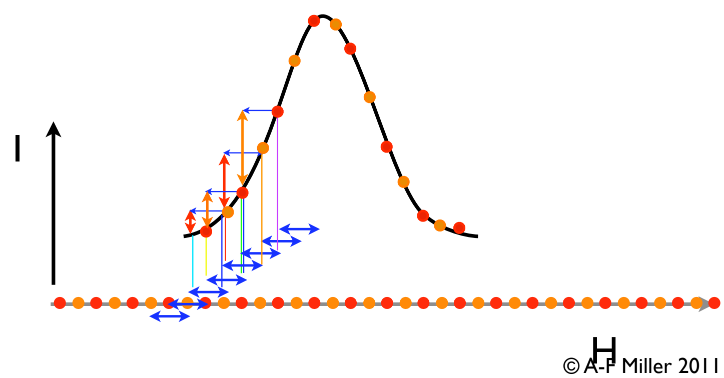


Field modulation with lock-in amplifier

Add to the swept field a small additional field oscillating at 100 kHz. This is called the field modulation δH.
Noise will fluctuate at random frequencies but the signal is now identified as that which fluctuates at 100 kHz. Only frequencies within 1 Hz of 1 kHz are collected.

At each average field value H_o, we record $\Delta I = I(H_o + \delta H/2) - I(H_o - \delta H/2)$, where δ is the magnitude of the field modulation.

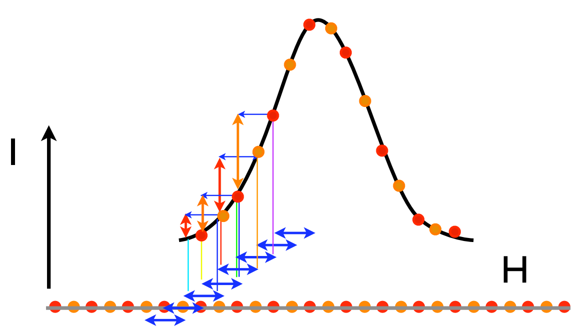
In the diagram these ΔI values are the vertical orange or red arrows.

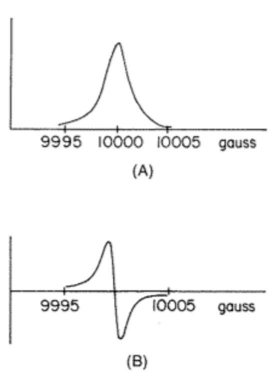


Field modulation with lock-in amplifier

Signal: detector current I varies with time, at same frequency as field oscillation and *in phase*. (Optimization of phase on the instrument.)

$\Delta I = I(H_o + \delta H/2) - I(H_o - \delta H/2)$ is measured as the centre field H_o is swept.





$$\lim_{(\delta H)\to 0} \frac{I(H_o + \frac{\delta H}{2}) - I(H_o - \frac{\delta H}{2})}{\delta H} = \frac{d(I)}{dH}$$

Fig. 9.4, Drago 1992

Distortion due to excessive field modulation amplitude

(δH is too big)

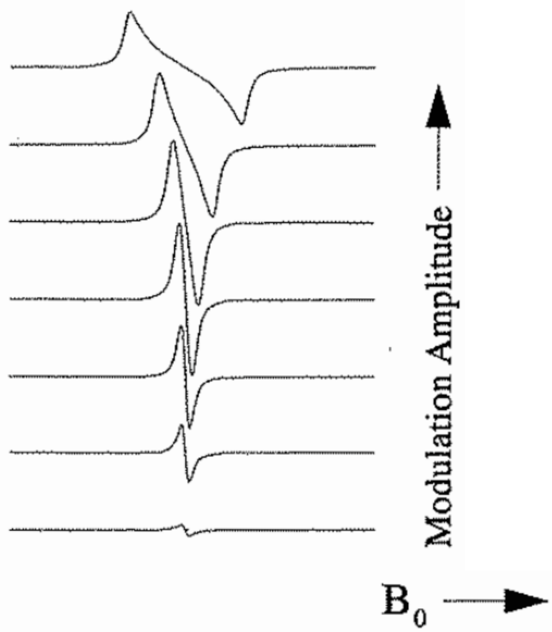


Fig. 2.15, Bruker EPR manual.

Integration to recover a familiar absorptive line

This EPR signal yields the above absorptive signal upon integration.

(Double integration is required to determine the area of signal and permit spin quantitation.)

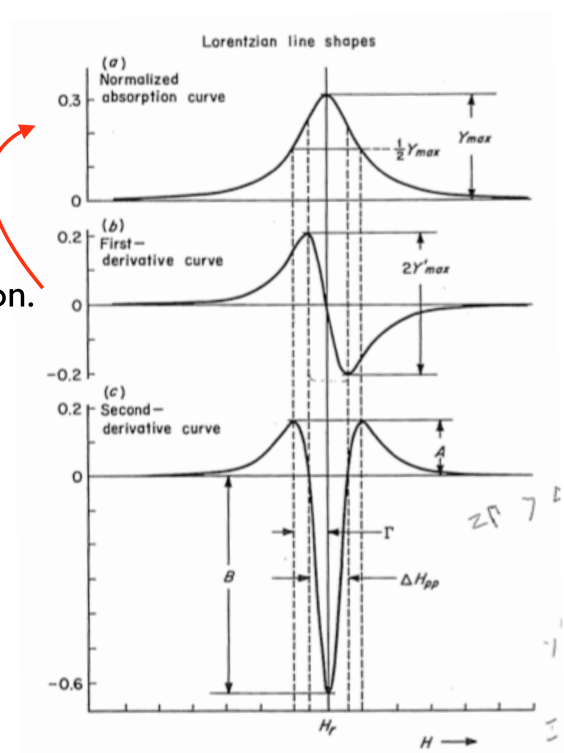


Fig. 2.9 Wertz and Bolton, 1986