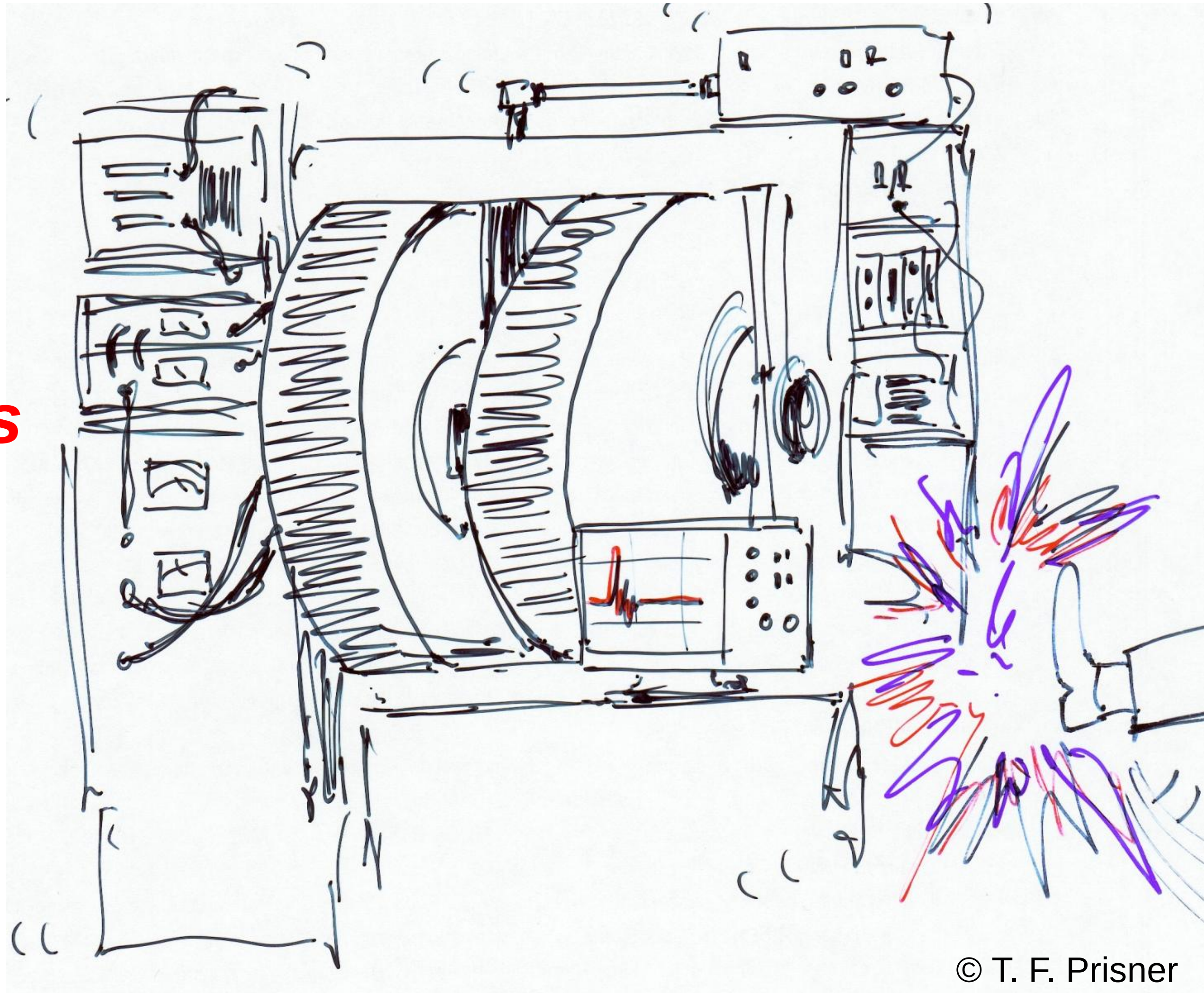
Electron Paramagnetic Resonance Spectroscopy

BASICS of CW-EPR

(CW: continuous waves)



What is EPR?

EPR is a spectroscopic technique that:

• detects unpaired electron spins (presence of unpaired electrons is mandatory)

• is nondestructive

• can be done in liquid or frozen solution, powders, crystals or gases

• yields structural and dynamical information

• needs for a standard experiment ~1 nmol of spins

• for a sample in solution: 30 µl sample (or less !)

of a concentration of ~100 µM paramagnetic species

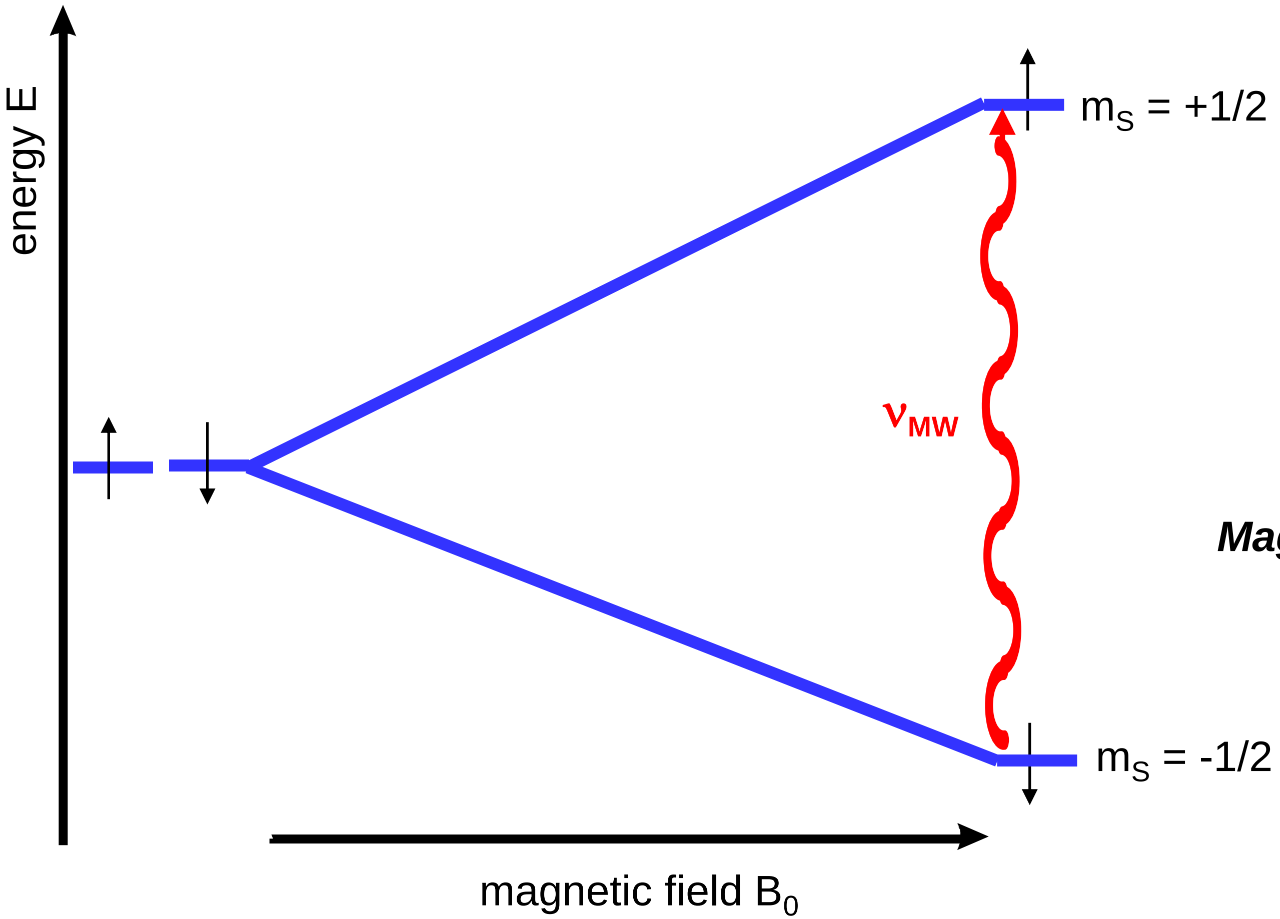
Where to find unpaired electrons?

- paramagnetic metal ions (Cu^{2+}, Mn^{2+}, Ni^{+}, Co^{2+}, Mo^{5+}, Fe^{2+}) e.g. in proteins and RNA
- metal cluster (FeS, Mn, Cu) e.g. in proteins or catalysis
- amino acid radicals of the protein backbone (tyrosine, triptophane, glycil, cystein)
- protein bound cofactor radicals (semiquinones and flavines)
- transient paramagnetic chromophores in light driven processes
- nitroxide spin labels attached to diamagnetic biomolecules
- defect centers in lattices
- unpaired electrons in semi- and superconductors
- stable organic high-spin radicals in molecular ferromagnets

In which research fields is EPR used?

- Physics: Susceptibility, Semiconductors, Quantum Dots, Defects, Quantum Computing…
- Chemistry: ET-Reaction Kinetics, Organometallics, Catalysis, Radicals, Photovoltaik…
- Biology: Enzymes, ET-Reactions, Folding&Dynamics, Metalloproteins, Structural Biology
- Radiology: Alanin radiation dosimetry, Radiation damage of DNA, food irradiation
- Material research: Polymers, Glases, Superconductors, Corrosion, Molecular Magnets...
- Archeology: dating...
- Geology: analysis of stones...

Magnetic Resonance Condition

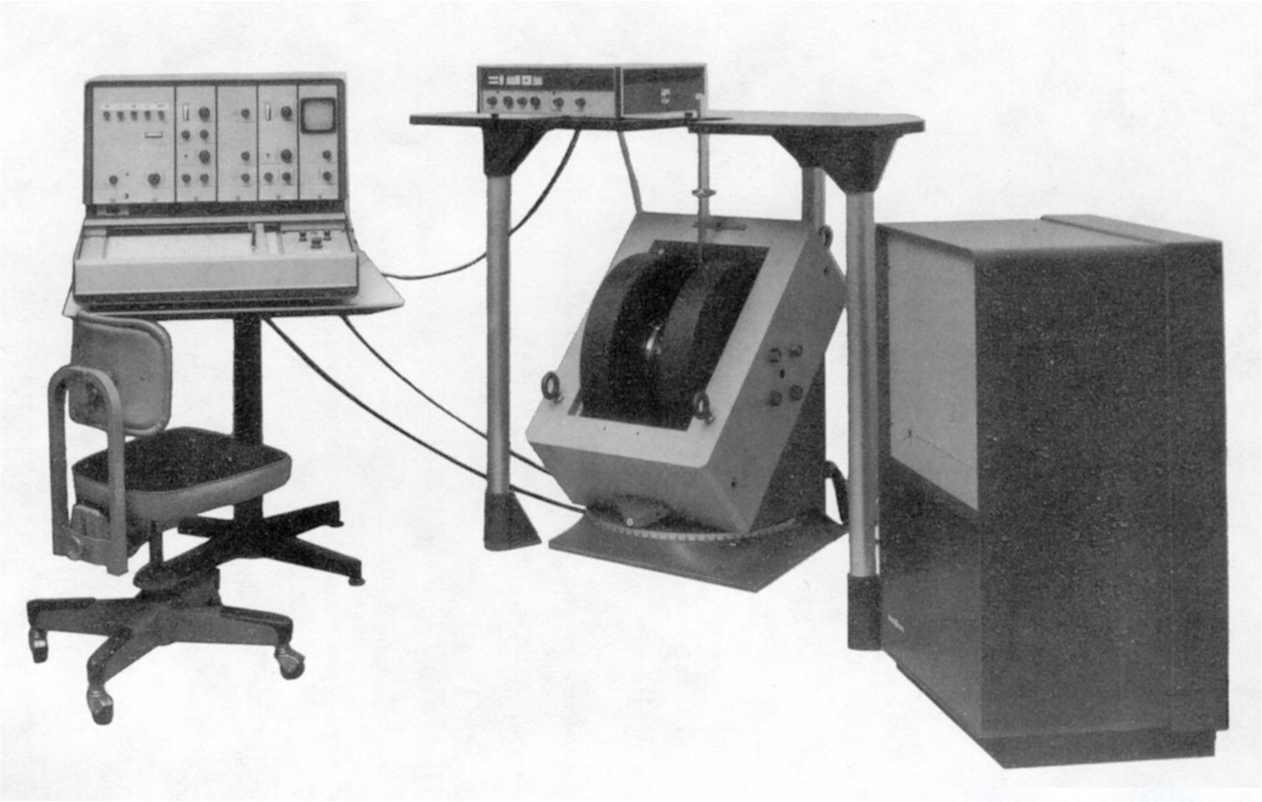


$$E = g \cdot \mu_B \cdot B_0 \cdot m_S$$

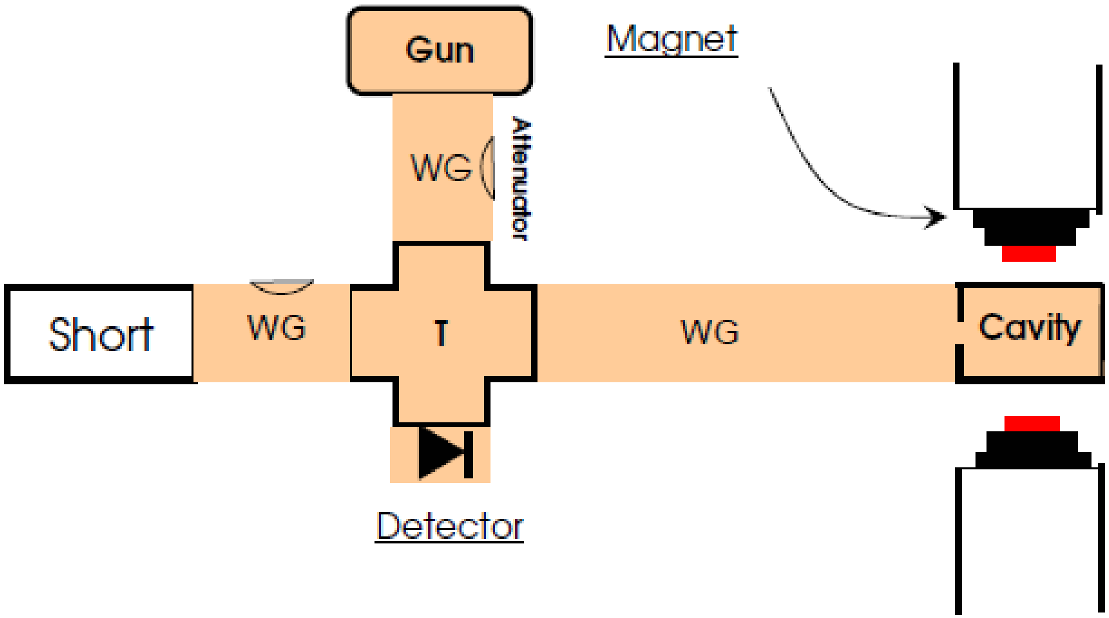
$$\Delta E = g \cdot \mu_B \cdot B_0 = h \cdot \nu$$

Magnetic Resonance Condition

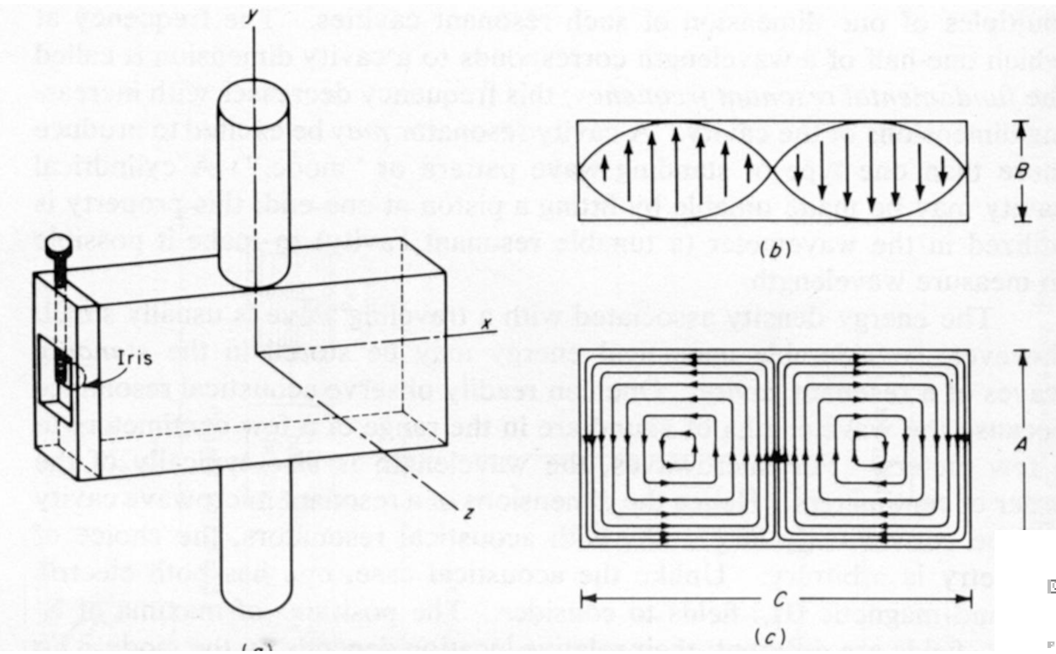
Schematic of a CW EPR-Spectrometer

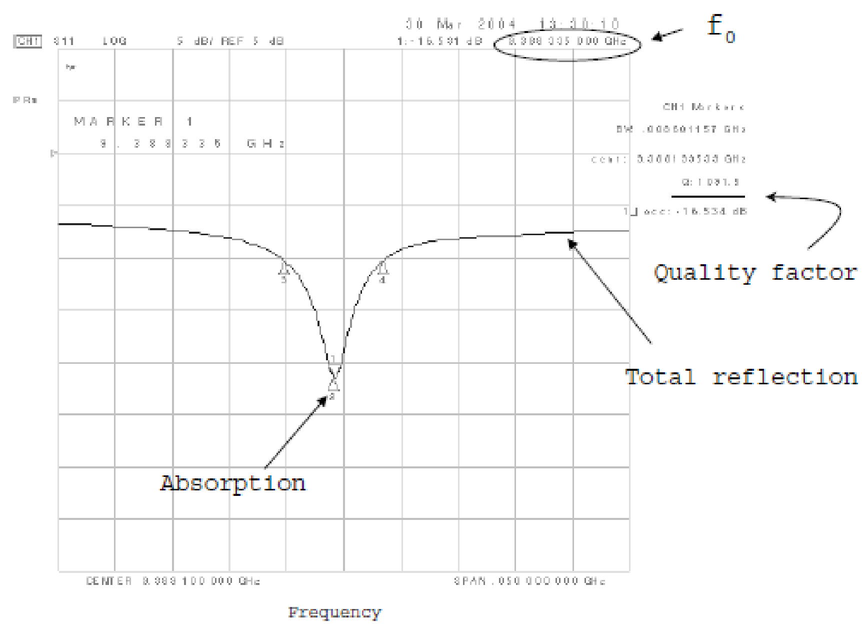


Block Diagram of a CW EPR-Spectrometer



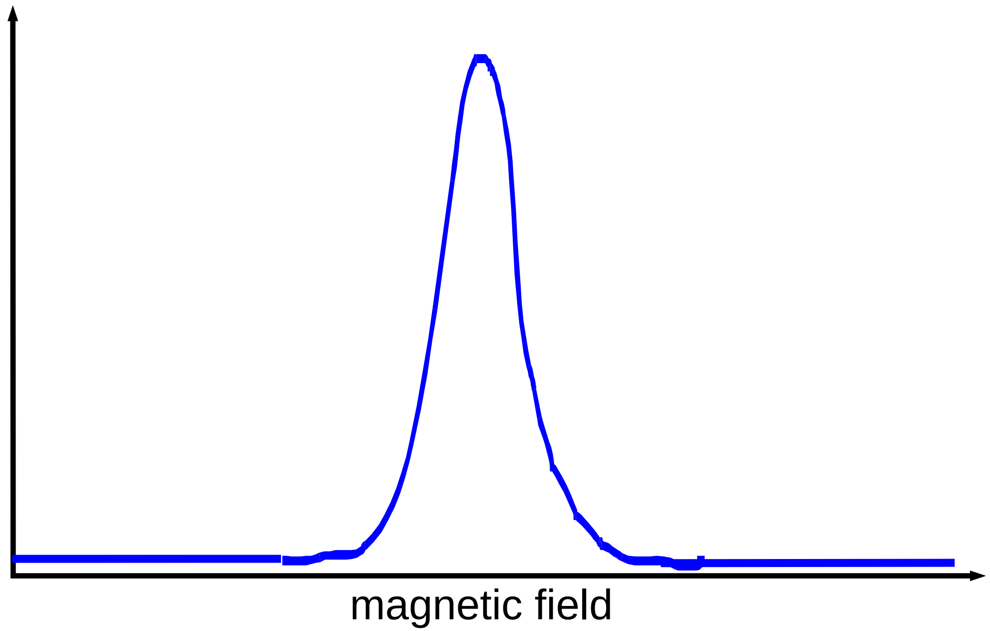
MW Resonator





Magnetic Resonance Condition

If that would be all, magnetic resonance spectroscopy NMR or EPR would only give:



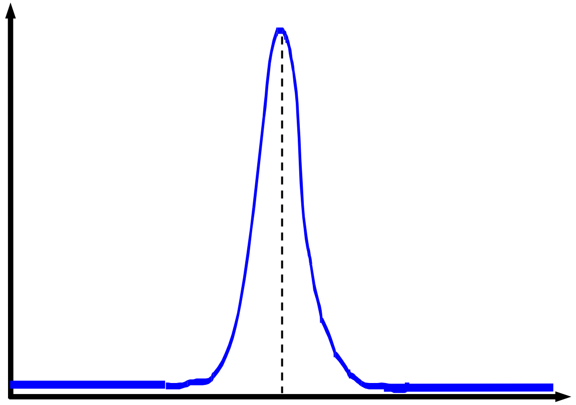
Everybody could go home and the DFG would have vasted Millions of Euros.

BUT:

Isotropic g-value

g is in EPR what the chemical shift is in NMR

$g = \text{const} * \nu\ (\text{MHz}) / B(\text{Gauss})$



$g_{free\ Electron} = 2.0023$

organic radicals $g_{iso} = 2.003 – 2.02$

metal centers $g_{iso} = 1.94\ (Mo^{V})$, 2-2.4 (Cu^{II}),

1.4-3.1 (Fe^{III})low spin,

2-10 (Fe^{III})high spin,

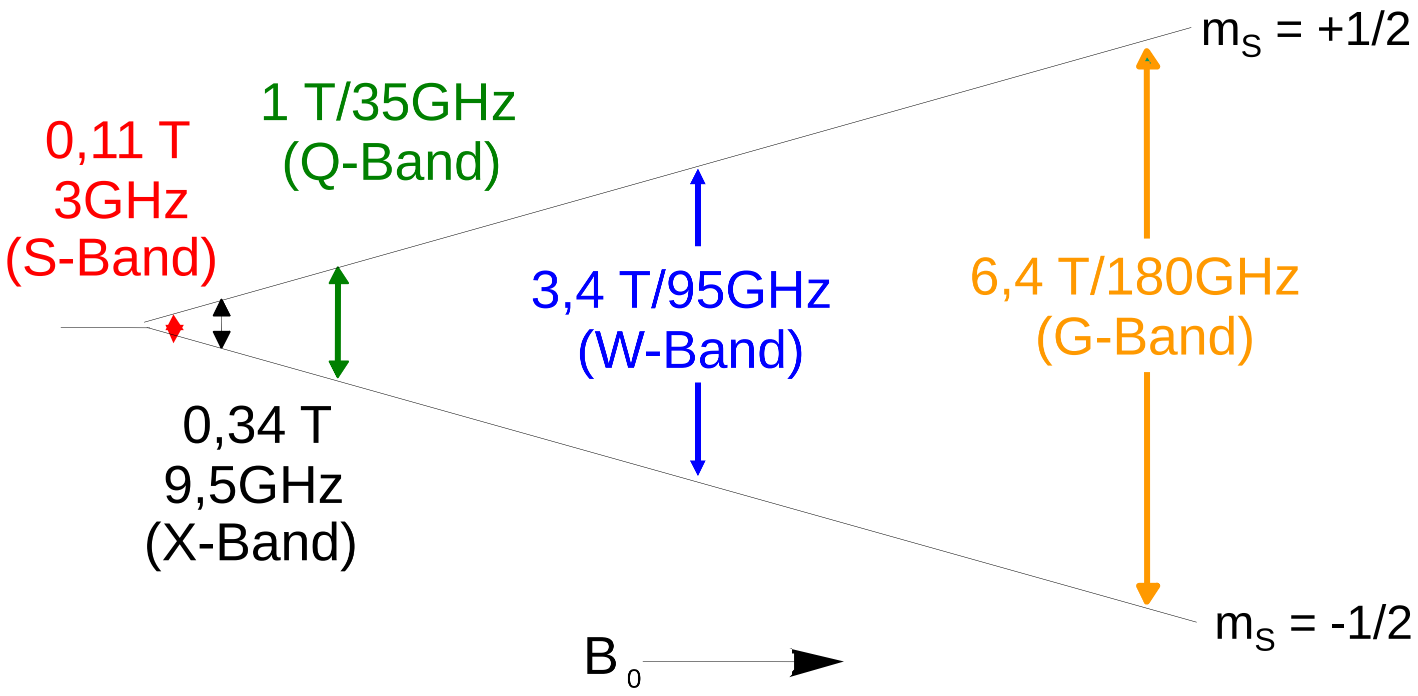
Ge 0.8-2

difference to g_{free} comes from spin-orbit coupling

NMR chemical shift only parts per million

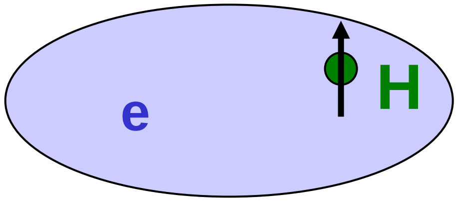
Still one line but shift on the magnetic field axis.

Microwave frequency bands and magnetic fields

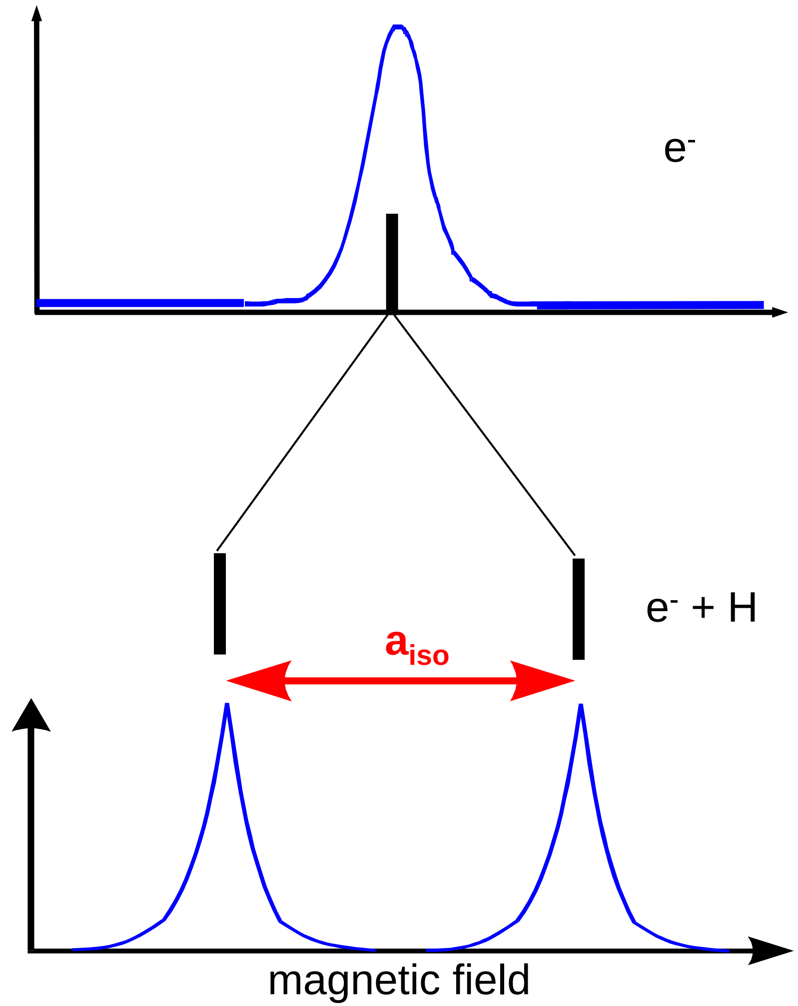


Isotropic Hyperfine Coupling

Electron spin density at the nucleus (Fermi contact interaction): isotropic a



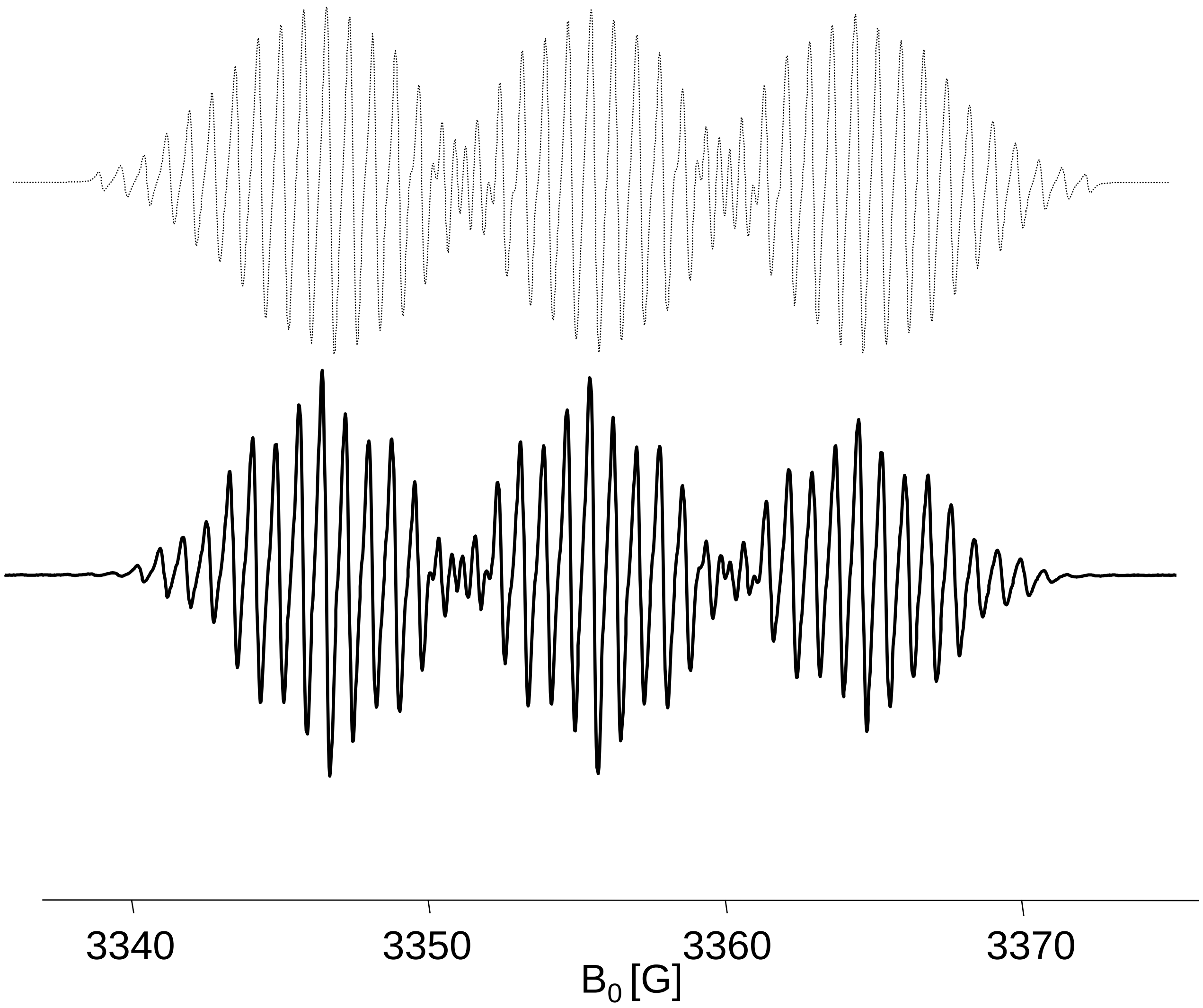
$I(^{1}H) = 1/2$

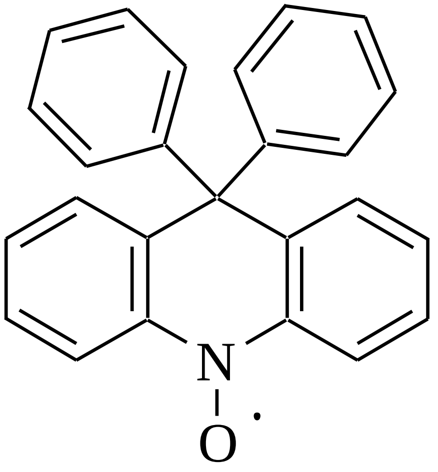


multiplicity rule:

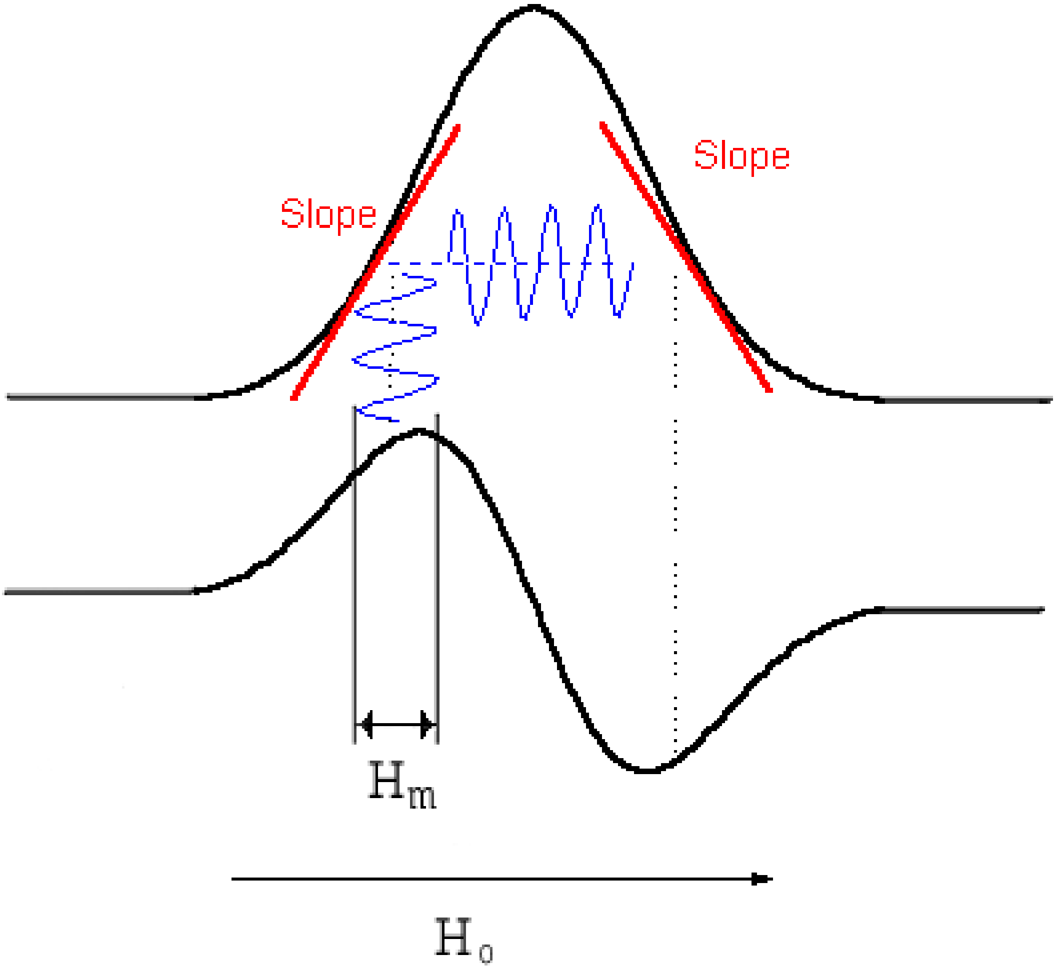
$L = 2 * n * I + 1$

Example for Isotropic Hyperfine Coupling





Field modulation technique



EPR Saturation

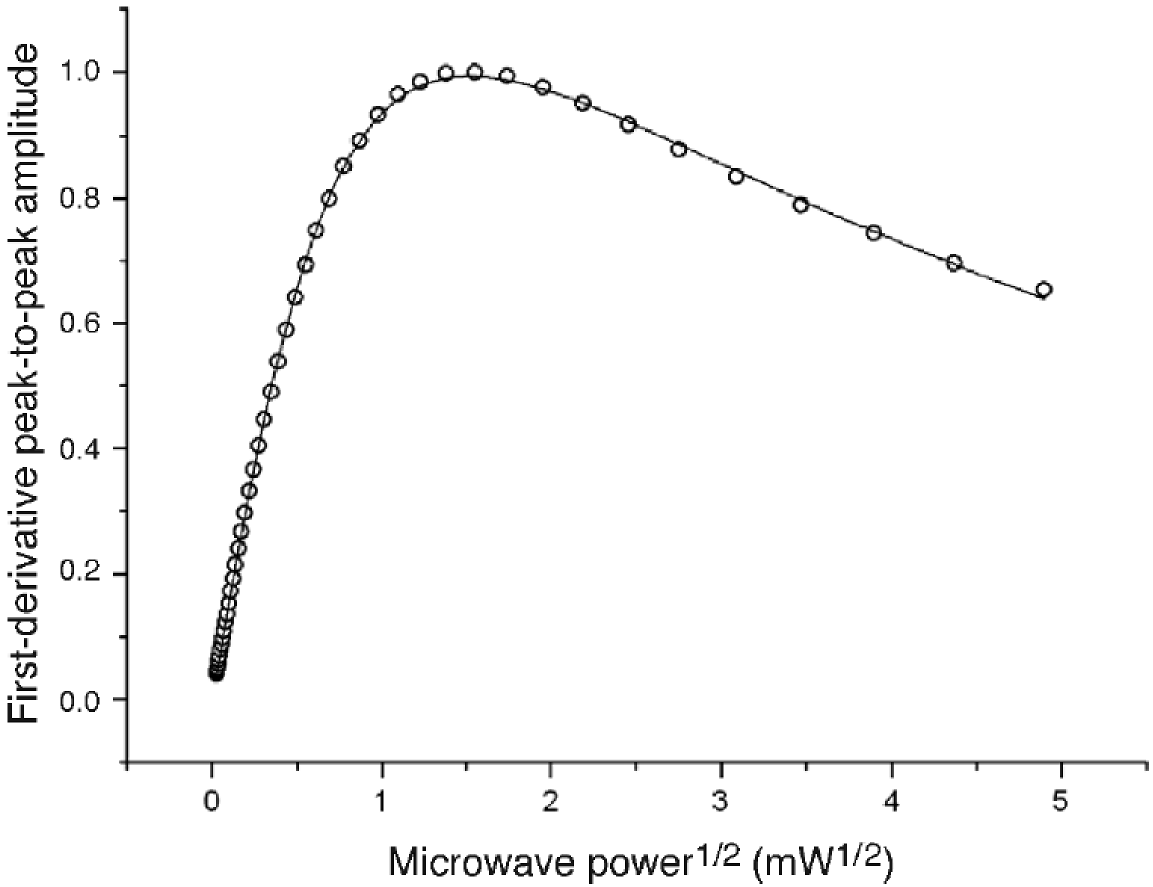


FIG. 2. Experimental data (○) and fitted saturation curve for a polycrystalline pellet of ammonium tartrate irradiated with a dose of 1 kGy. The magnetic field was modulated at 750 Hz.

From:
Lund et al. Radiation Research 172 (2009)