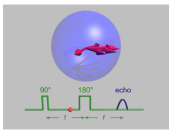
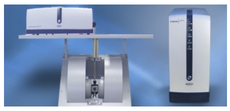
Electron Paramagnetic Resonance and Dynamic Nuclear Polarisation

AS:MIT CH916

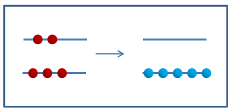


Gavin W Morley,
Department of Physics,
University of Warwick

Overview

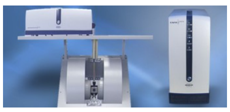


Electron paramagnetic resonance
- What it is
- Why it's useful



Dynamic nuclear polarization
- Why it's useful
- What it is

Electron paramagnetic resonance (EPR)

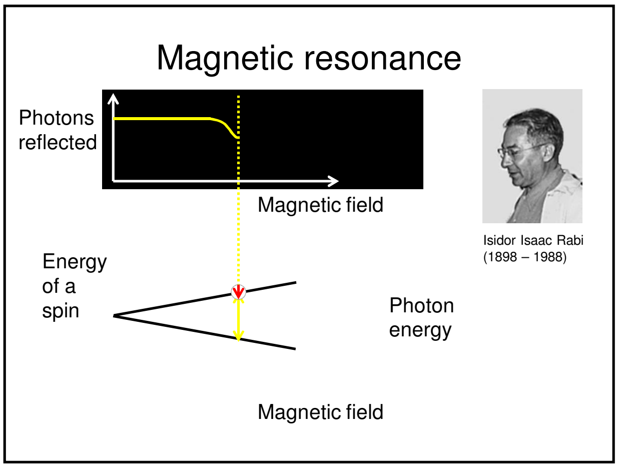


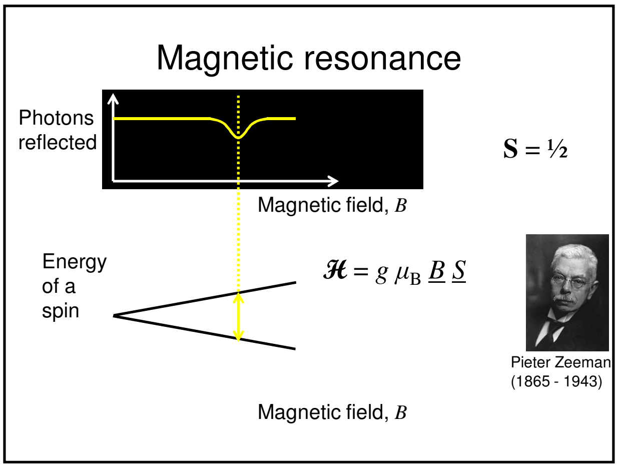
…NMR for electrons:
The crucial difference is that the electron magnetic moment is 660 times larger than that of a proton

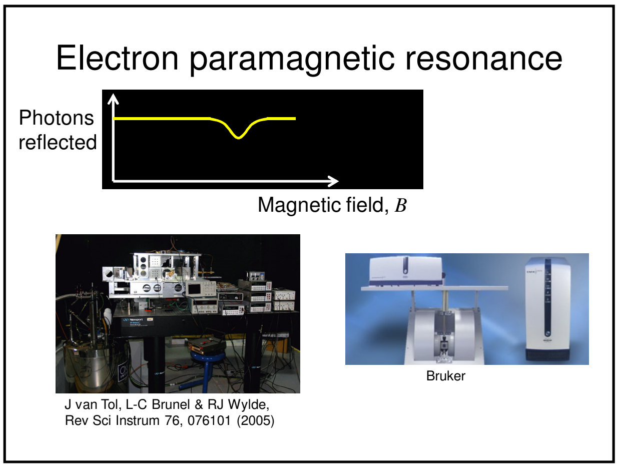
Also known as
… electron spin resonance (ESR)
… or electron magnetic resonance (EMR)
… or ferromagnetic resonance (FMR)

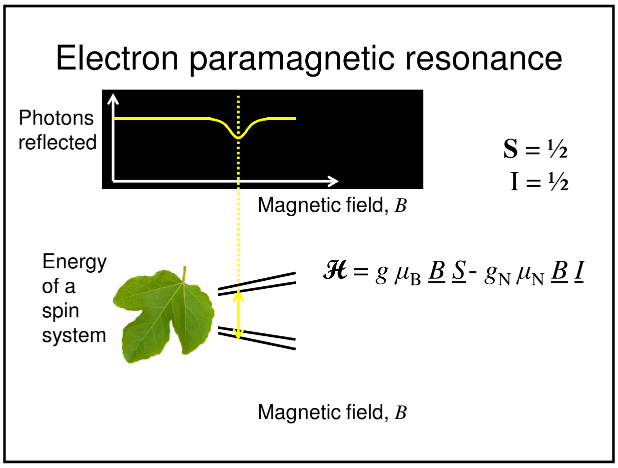
Magnetism

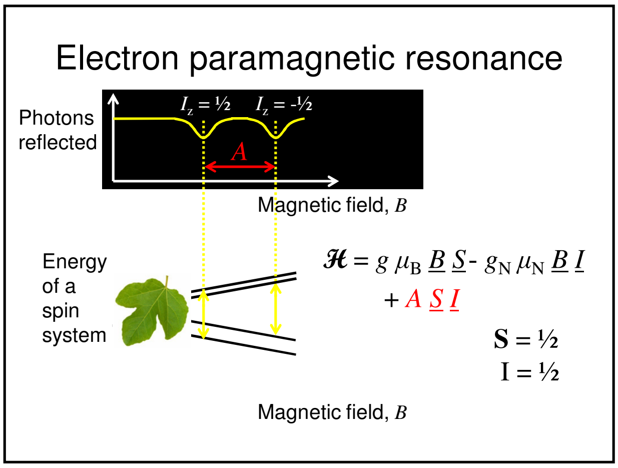
	Electron spins tend to:
Paramagnetism:	follow
Diamagnetism:	oppose
Ferromagnetism:	ignore
	…an applied magnetic field


Magnetic resonance
Photons reflected
Magnetic field
Energy of a spin
Photon energy
Magnetic field
Isidor Isaac Rabi (1898 – 1988)

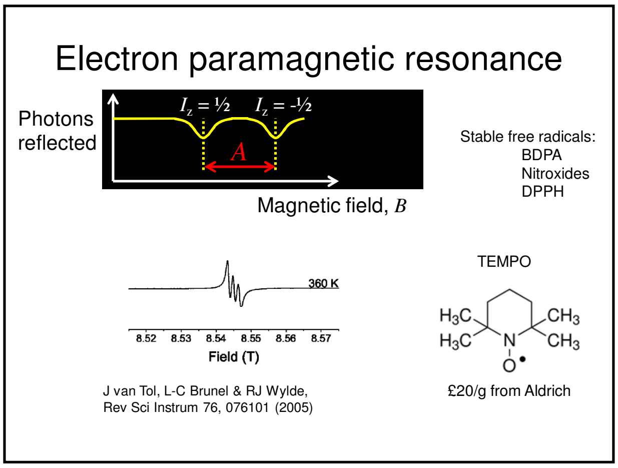

Magnetic resonance
Photons reflected
Magnetic field, B
$S = ½$
Energy of a spin
$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S}$
Pieter Zeeman (1865 - 1943)
Magnetic field, B


Electron paramagnetic resonance
Photons reflected
Magnetic field, B
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)
Bruker

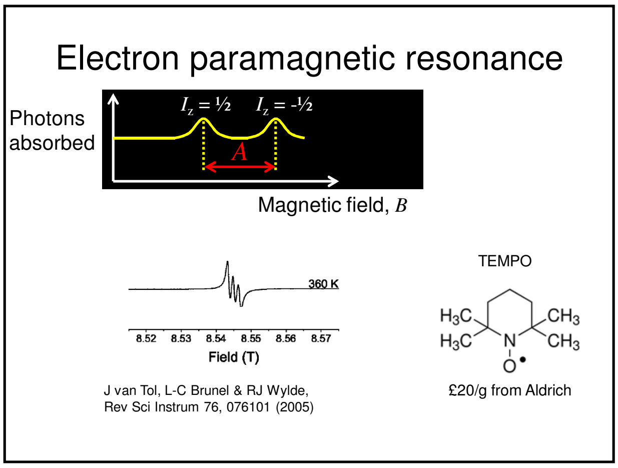

Electron paramagnetic resonance
Photons reflected
Magnetic field, B
$S = ½$
$I = ½$
Energy of a spin system
$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I}$
Magnetic field, B



Electron paramagnetic resonance
Photons reflected
$I_z = ½$ $I_z = -½$
A
Magnetic field, B
Energy of a spin system
$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I}$
$+ A\,\underline{S}\,\underline{I}$
S = ½
I = ½
Magnetic field, B



Electron paramagnetic resonance
Photons reflected
$I_z = ½$ $I_z = -½$
A
Magnetic field, B
Stable free radicals:
BDPA
Nitroxides
DPPH
360 K
8.52 8.53 8.54 8.55 8.56 8.57
Field (T)
J van Tol, L-C Brunel & RJ Wylde,
Rev Sci Instrum 76, 076101 (2005)
TEMPO
H_3C H_3C N CH_3 CH_3 O•
£20/g from Aldrich



Electron paramagnetic resonance
Photons absorbed
$I_z = ½$ $I_z = -½$
A
Magnetic field, B
360 K
8.52 8.53 8.54 8.55 8.56 8.57
Field (T)
J van Tol, L-C Brunel & RJ Wylde,
Rev Sci Instrum 76, 076101 (2005)
TEMPO
H_3C H_3C N CH_3 CH_3 O•
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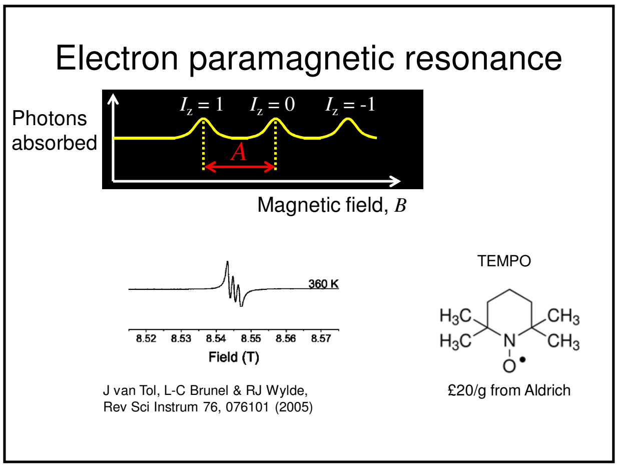

Electron paramagnetic resonance
Photons absorbed
$I_z = 1$ $I_z = 0$ $I_z = -1$
A
Magnetic field, B
360 K
8.52 8.53 8.54 8.55 8.56 8.57
Field (T)
J van Tol, L-C Brunel & RJ Wylde,
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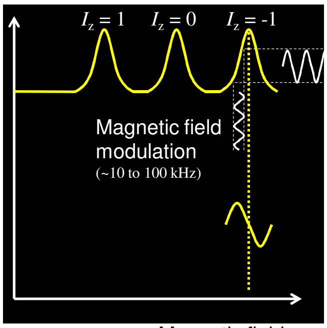
TEMPO
H_3C H_3C N CH_3 CH_3 O•
£20/g from Aldrich

Electron paramagnetic resonance

Photons absorbed



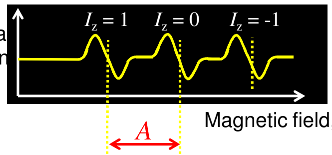
Differential absorption

Magnetic field, B

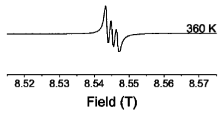
Advantage: noise only at modulation frequency

Electron paramagnetic resonance

Differential absorption

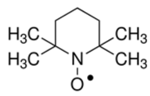


Magnetic field, B



J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)

TEMPO

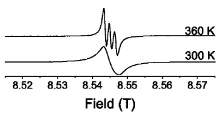


£20/g from Aldrich

Electron paramagnetic resonance

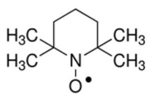
Motional narrowing occurs due to molecular rotation at higher temperature

Magic angle spinning is not used in EPR because you can't spin fast enough



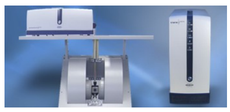
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)

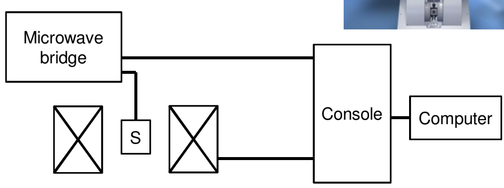
TEMPO



£20/g from Aldrich

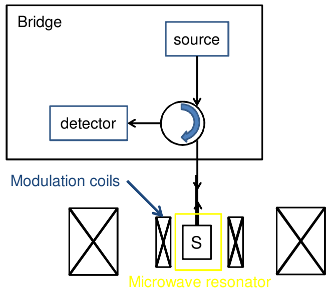
Electron paramagnetic resonance spectrometer

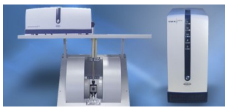




Electromagnet (up to 1.5 T) or superconducting magnet for higher field

Electron paramagnetic resonance spectrometer



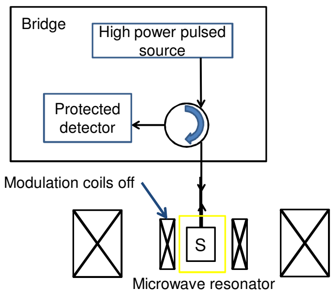


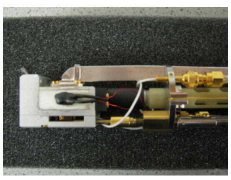
Electron paramagnetic resonance spectrometer

Continuous-wave (CW) EPR so far…

Pulsed EPR next

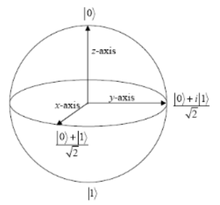
Pulsed electron paramagnetic resonance spectrometer



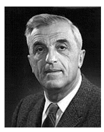


Bruker probe

Pulsed electron paramagnetic resonance

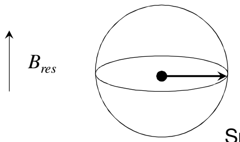


Bloch sphere



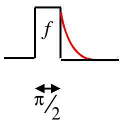
Felix Bloch (1905-1983)
Photo courtesy Stanford News Service

Pulsed electron paramagnetic resonance



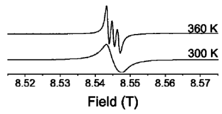
resonance condition
$g\ \mu_B\ B_{res} = h\ f$

Spins polarize (thermalize) on timescale T_1



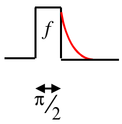
Free induction decay (FID) on timescale T_2^*

Pulsed EPR



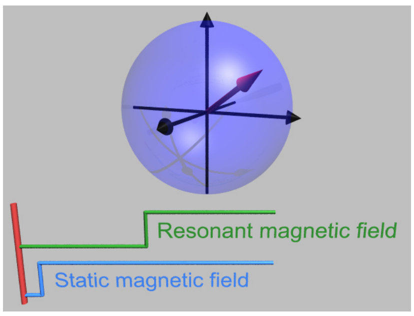
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)

↔
~100 MHz width
Pulse width < 500 MHz
Resonator ringing → deadtime
Short T_2 and T_2^* compared to NMR

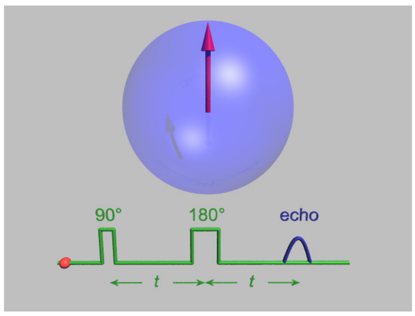


Homogeneous (T_2) can be much longer than inhomogeneous (T_2^*) so most pulsed EPR uses spin echo

Rotating Frame

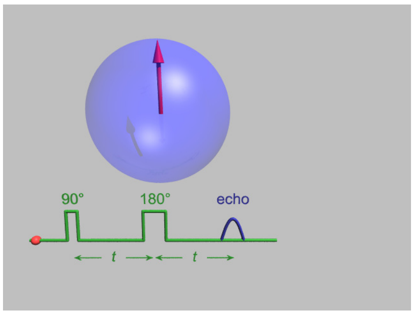


Spin echo



In rotating frame

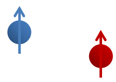
Spin echo decay



Erwin L Hahn (born 1921)
Photo: AIP Emilio Segre Visual Archives, Stephen Jacobs Collection

Pulsed EPR

Double electron-electron resonance (DEER) allows distances between two electron spins in the range 2 to 6 nm to be measured (cf < 1 nm by NMR for two nuclear spins)

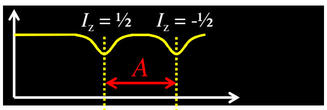


Dipolar coupling α $1/r^3$

Site directed spin labelling with one or more TEMPO

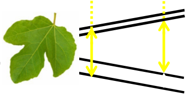
Electron nuclear double resonance (ENDOR)

Photons reflected



Magnetic field, B

Energy of a spin system



$$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I} + A\,\underline{S}\,\underline{I}$$

$S = ½$

$I = ½$

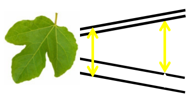
Magnetic field, B

Electron nuclear double resonance (ENDOR)

Why do ENDOR instead of NMR?

- only need ~10^{10} spins instead of ~10^{15}
- NMR may be difficult near the electron spin

Energy of a spin system



$$\mathcal{H} = g\,\mu_B\,\underline{B_0}\,\underline{S} - g_N\,\mu_N\,\underline{B_0}\,\underline{I} + A\,\underline{S}\,\underline{I}$$

$S = ½$

$I = ½$

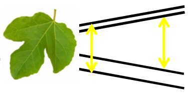
Magnetic field, B_0

Electron nuclear double resonance (ENDOR)

EPR language: B_0 is static magnetic field
B_1 is EPR magnetic field
B_2 is NMR magnetic field

(NMR language: B_1 is NMR magnetic field)

Energy of a spin system



$$\mathcal{H} = g\,\mu_B\,\underline{B_0}\,\underline{S} - g_N\,\mu_N\,\underline{B_0}\,\underline{I} + A\,\underline{S}\,\underline{I}$$

S = ½
I = ½

Magnetic field, B_0

ENDOR for quantum computing

Classical computer	Quantum computer
Bits	Qubits
0 or 1	$\alpha\,\lvert 0\rangle + \beta\,\lvert 1\rangle$

Spin qubits in silicon

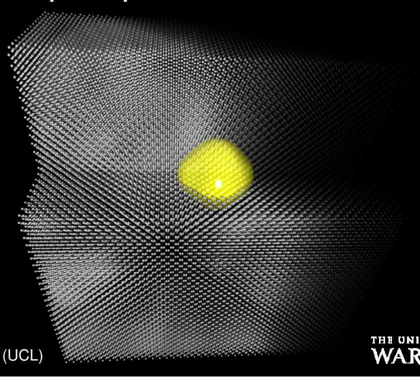
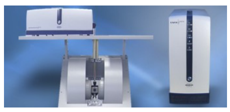


Image by Manuel Vögtli (UCL)

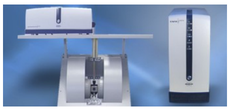
THE UNIVERSITY OF WARWICK

Other EPR applications

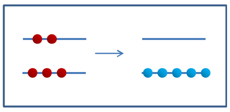


- Quality control in beer, wine etc
- Radiation dose received by teeth

Overview

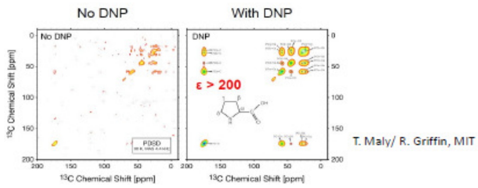


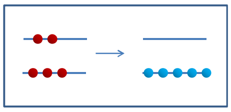
Electron paramagnetic resonance
- What it is
- Why it's useful



Dynamic nuclear polarization
- Why it's useful
- What it is

Dynamic nuclear polarization (DNP)





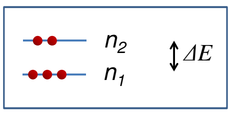
Dynamic nuclear polarization
- More signal

Dynamic nuclear polarization (DNP)

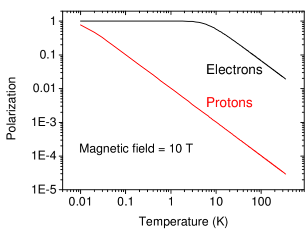
$$\frac{n_2}{n_1} = e^{-\frac{\Delta E}{k_B T}}$$

Boltzmann polarization:

$$P = \frac{n_1 - n_2}{n_1 + n_2}$$



Dynamic nuclear polarization (DNP)

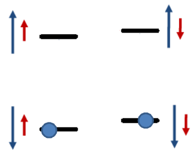


Boltzmann polarization:

$$P = \frac{n_1 - n_2}{n_1 + n_2}$$

So transfer electronic polarization to nuclei

Dynamic nuclear polarization (DNP)



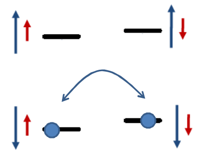
Initial polarizations:

Electrons > 95%
Nuclei < 0.1%

For 8.6 T and 3 K

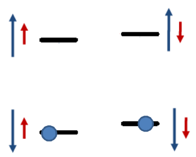
Dynamic nuclear polarization (DNP)

Nuclear magnetic resonance (NMR)



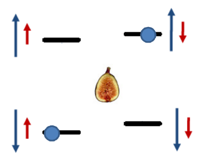
Dynamic nuclear polarization (DNP)

Electron paramagnetic resonance (EPR)



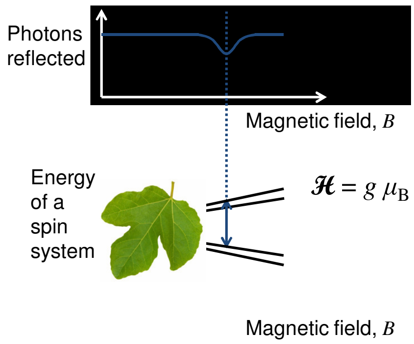
Dynamic nuclear polarization (DNP)

Electron paramagnetic resonance (EPR)



Forbidden transitions: zero quantum and double quantum

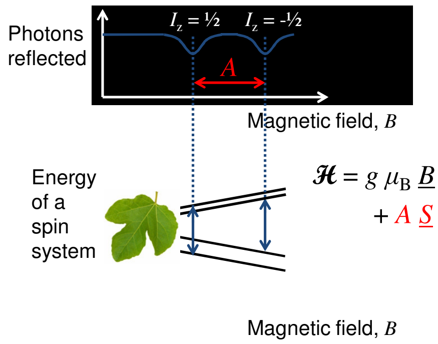
Magnetic resonance



$$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I}$$

S = ½
I = ½

Magnetic resonance



Gregory Breit
(1899-1981)

$$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I} + A\,\underline{S}\,\underline{I}$$

S = ½
I = ½

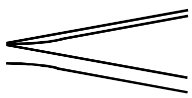
Magnetic resonance

Energy of a spin system

Breit-Rabi diagram

Triplet, F = 1: ↑↑
(↑↓ + ↓↑)/√2
↓↓

Singlet, F = 0: (↑↓ - ↓↑)/√2



Magnetic field, B

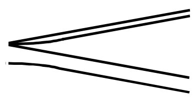
$$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I} + A\,\underline{S}\,\underline{I}$$

Magnetic resonance

Energy of a spin system

$$A\,\underline{S}\,\underline{I} = {}^{A}\!/_{2}\,(S^{+} I^{-} + S^{-} I^{+}) + A\,S_z\,I_z$$

$$S^{\pm} = S_x \pm i\,S_y$$

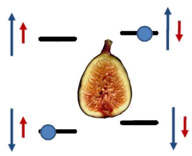


Magnetic field, B

$$\mathcal{H} = g\,\mu_B\,\underline{B}\,\underline{S} - g_N\,\mu_N\,\underline{B}\,\underline{I} + A\,\underline{S}\,\underline{I}$$

Dynamic nuclear polarization (DNP)

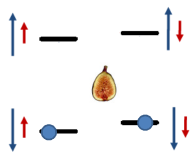
Electron paramagnetic resonance (EPR)



more
Forbidden
at high magnetic fields

Dynamic nuclear polarization (DNP)

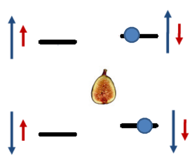
Solid effect DNP



also gets weaker at high magnetic fields

Dynamic nuclear polarization (DNP)

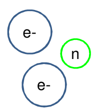
Solid effect DNP



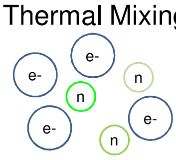
also gets weaker at high magnetic fields

Dynamic nuclear polarization (DNP)

Cross effect

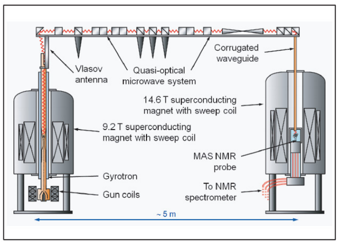


Thermal Mixing



also get weaker at high magnetic fields

Dynamic nuclear polarization (DNP)



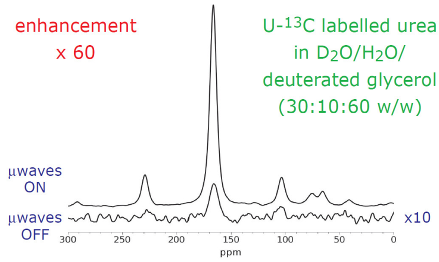
Gyrotron DNP pioneered
By Bob Griffin's group
at MIT

KJ Pike *et al.*, J Mag Res 215, 1 (2012)
See also Bruker's 263 GHz AVANCE™

Dynamic nuclear polarization (DNP)

enhancement
x 60

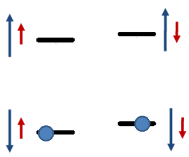
U-^{13}C labelled urea
in D_2O/H_2O/
deuterated glycerol
(30:10:60 w/w)



Ray Dupree, Steven Brown, Mark Newton, Kevin Pike, Andrew Howes,
Tom Kemp, Mark Smith *et al.* at Warwick,
see KJ Pike *et al.*, J Mag Res 215, 1 (2012)

Dynamic nuclear polarization (DNP)

EPR + NMR = Electron nuclear double resonance (ENDOR)

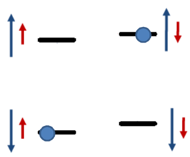


ENDOR-DNP:

A S Brill, PRA 66 043405 (2003)

Dynamic nuclear polarization (DNP)

EPR + NMR = Electron nuclear double resonance (ENDOR)

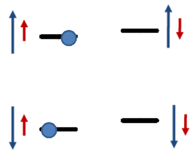


ENDOR-DNP:

A S Brill, PRA 66 043405 (2003)

Dynamic nuclear polarization (DNP)

EPR + NMR = Electron nuclear double resonance (ENDOR)



ENDOR-DNP:

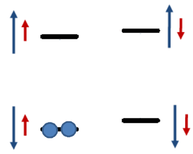
A S Brill, PRA 66 043405 (2003)

Background Our research

Dynamic nuclear polarization (DNP)

GWM, J van Tol, A Ardavan, K Porfyrakis, J Zhang & GAD Briggs, PRL 98, 20501 (2007)

GWM, K Porfyrakis, A Ardavan & J van Tol, AMR 34, 347 (2008)



ENDOR-DNP:

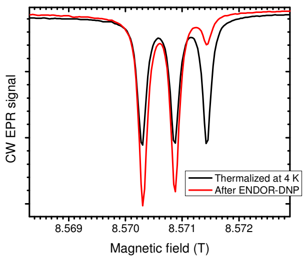
A S Brill, PRA 66 043405 (2003)

See also: B Epel, A Poppl, P Manikandan, S Vega & D Goldfarb, JMR 148 388 (2001)

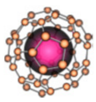
Background Our research

Dynamic nuclear polarization

240 GHz excitation, $A/\hbar = 16$ MHz

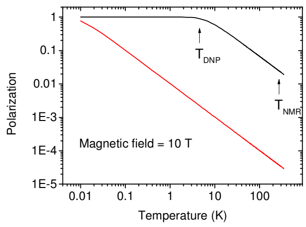


ENDOR-DNP at 4 K



Dynamic nuclear polarization

Temperature jump



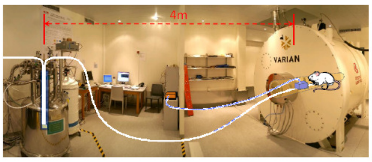
gain x50 from DNP and x200 from temp → x10,000 total

See Ardenkjaer-Larsen et al, PNAS 100, 10158 (2003)

Dynamic nuclear polarization

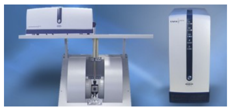
Temperature jump with dissolution

- Actively shielded 9.4T imager within 4m of DNP setup
- Delay between dissolution and infusion: 3 s
- Hyperpolarized liquid is transferred into a remotely-controlled infusion pump located inside the magnet bore

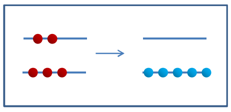


Arnaud Comment and Rolf Gruetter, Lausanne

Conclusions



EPR history: first observed in 1944 by Zavoisky in Kazan State University and developed independently at the same time by Bleaney at Oxford University.
Basic textbook: Weil, Bolton & Wertz, Electron paramagnetic resonance, Wiley (1994).
Pulsed EPR textbook: Schweiger & Jeschke, Principles of pulse EPR, OUP 2001.



Dynamic nuclear polarization
For a review see: T Maly *et al.*, DNP at high magnetic fields, Journal of Chemical Physics, 128, 052211 (2008)