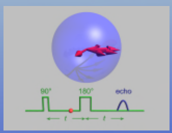
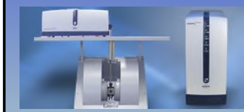
Electron Paramagnetic Resonance and Dynamic Nuclear Polarisation

CH916

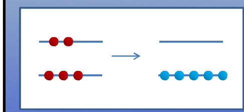


Gavin W Morley,
Department of Physics,
University of Warwick

Overview

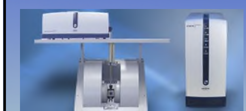


Electron paramagnetic resonance
- What it is
- Why it's useful

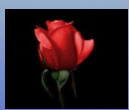


Dynamic nuclear polarization
- Why it's useful
- What it is

Electron paramagnetic resonance (EPR)



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



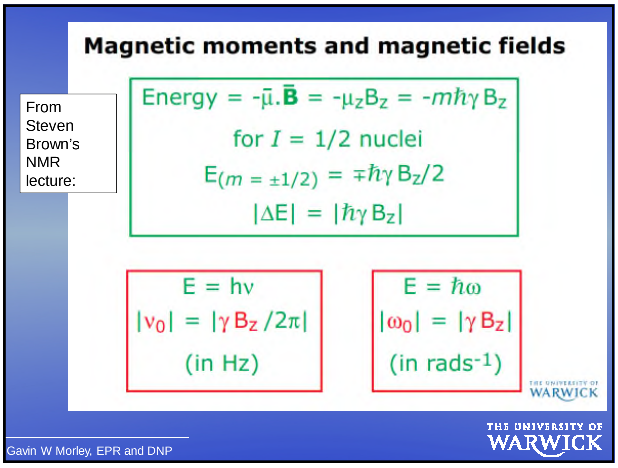
EPR is NMR for electrons

Magnetism

Electron spins tend to:

Paramagnetism: follow
Diamagnetism: oppose
Ferromagnetism: ignore

…an applied magnetic field


Magnetic moments and magnetic fields
From Steven Brown's NMR lecture:
Energy = $-\bar{\mu}.\bar{\mathbf{B}} = -\mu_z B_z = -m\hbar\gamma B_z$
for I = 1/2 nuclei
$E(m = \pm 1/2) = \mp\hbar\gamma B_z/2$
$|\Delta E| = |\hbar\gamma B_z|$
$E = h\nu$
$|\nu_0| = |\gamma B_z/2\pi|$
(in Hz)
$E = \hbar\omega$
$|\omega_0| = |\gamma B_z|$
(in rads^{-1})
Gavin W Morley, EPR and DNP
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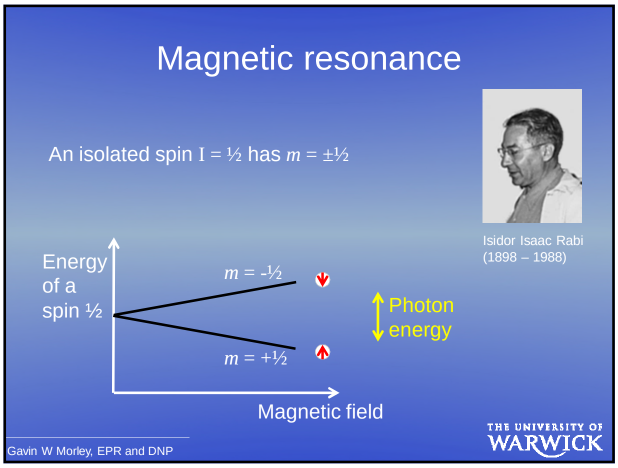
Magnetic resonance
An isolated spin I = ½ has $m = \pm$½
Isidor Isaac Rabi
(1898 – 1988)
Energy of a spin ½
m = -½
m = +½
Photon energy
Magnetic field
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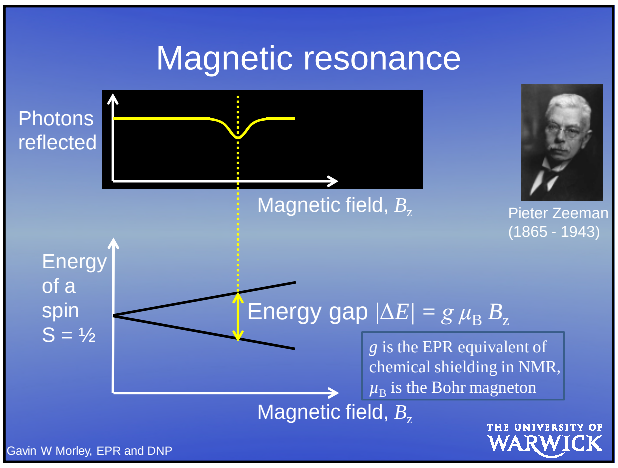
Magnetic resonance
Photons reflected
Magnetic field, B_z
Pieter Zeeman
(1865 - 1943)
Energy of a spin S = ½
Energy gap $|\Delta E| = g\,\mu_B\,B_z$
g is the EPR equivalent of chemical shielding in NMR, μ_B is the Bohr magneton
Magnetic field, B_z
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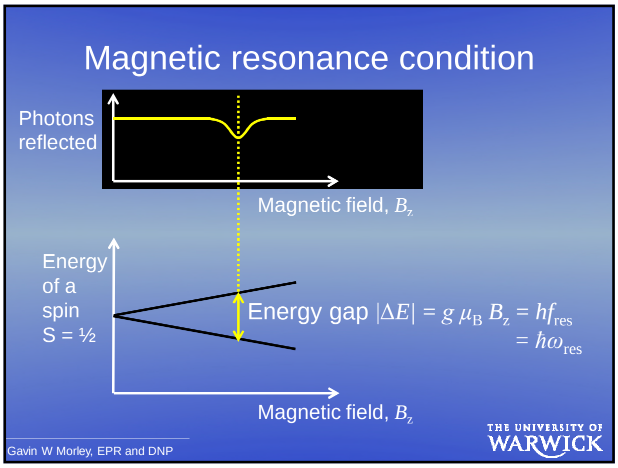
Magnetic resonance condition
Photons reflected
Magnetic field, B_z
Energy of a spin S = ½
Energy gap $|\Delta E| = g\,\mu_B\,B_z = hf_{res}$
$= \hbar\omega_{res}$
Magnetic field, B_z
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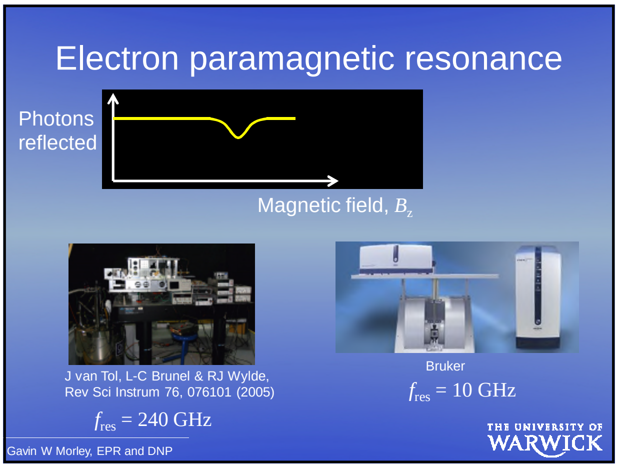
Electron paramagnetic resonance
Photons reflected
Magnetic field, B_z
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)
f_{res} = 240 GHz
Bruker
f_{res} = 10 GHz
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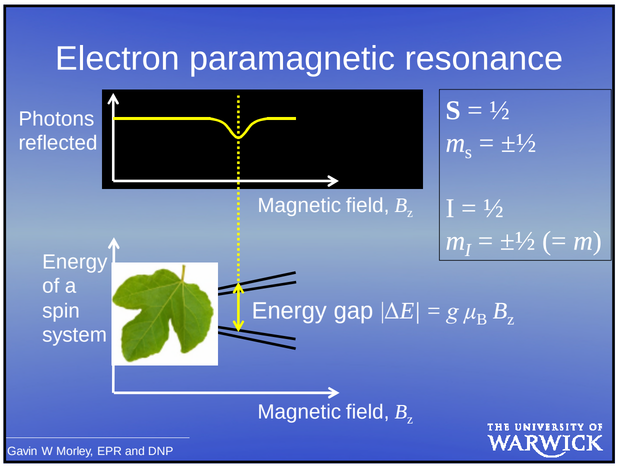
Electron paramagnetic resonance
Photons reflected
Magnetic field, B_z
S = ½
m_s = ±½
I = ½
m_I = ±½ (= m)
Energy of a spin system
Energy gap $|\Delta E| = g\,\mu_B\,B_z$
Magnetic field, B_z
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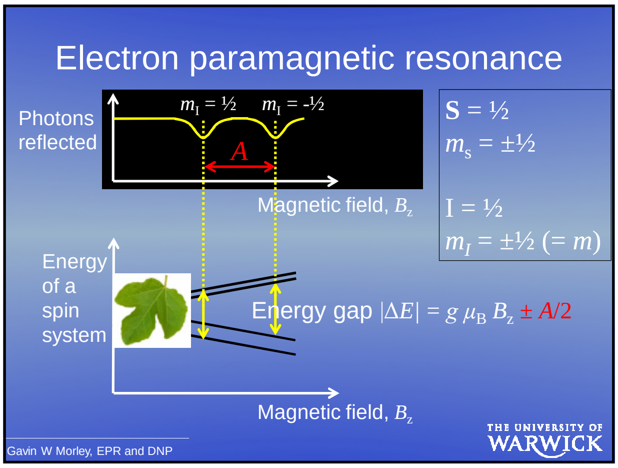
Electron paramagnetic resonance
Photons reflected
m_I = ½ m_I = -½
A
Magnetic field, B_z
S = ½
m_s = ±½
I = ½
m_I = ±½ (= m)
Energy of a spin system
Energy gap $|\Delta E| = g\,\mu_B\,B_z \pm A/2$
Magnetic field, B_z
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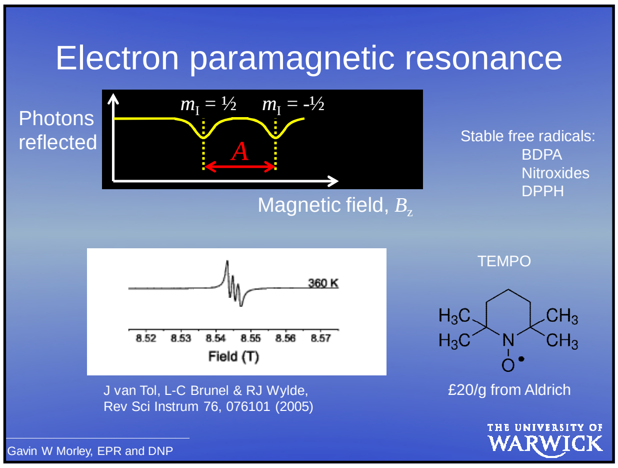
Electron paramagnetic resonance
Photons reflected
m_I = ½ m_I = -½
A
Magnetic field, B_z
Stable free radicals:
BDPA
Nitroxides
DPPH
360 K
8.52 8.53 8.54 8.55 8.56 8.57
Field (T)
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)
TEMPO
H_3C CH_3 H_3C CH_3 N O
£20/g from Aldrich
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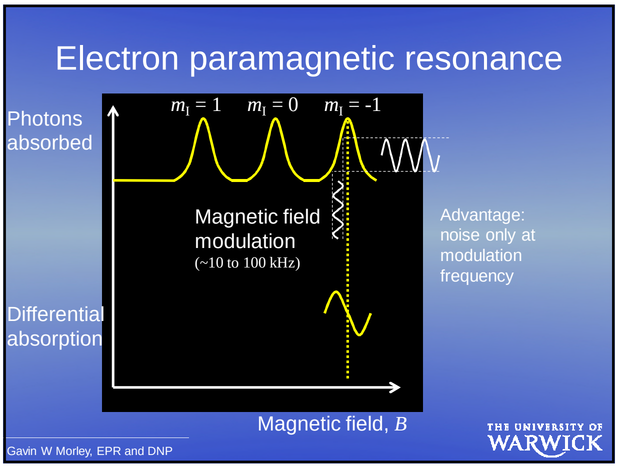
Electron paramagnetic resonance
Photons absorbed
$m_I = 1$ $m_I = 0$ $m_I = -1$
Magnetic field modulation
(~10 to 100 kHz)
Advantage: noise only at modulation frequency
Differential absorption
Magnetic field, B
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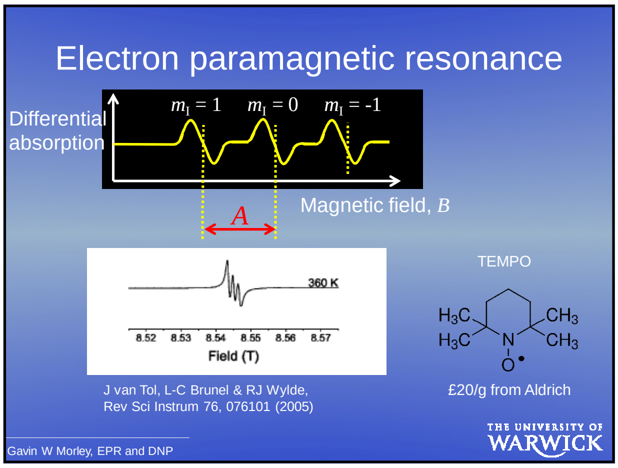
Electron paramagnetic resonance
Differential absorption
$m_I = 1$ $m_I = 0$ $m_I = -1$
A
Magnetic field, B
360 K
8.52 8.53 8.54 8.55 8.56 8.57
Field (T)
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)
TEMPO
H_3C CH_3 H_3C N CH_3 O•
£20/g from Aldrich
Gavin W Morley, EPR and DNP
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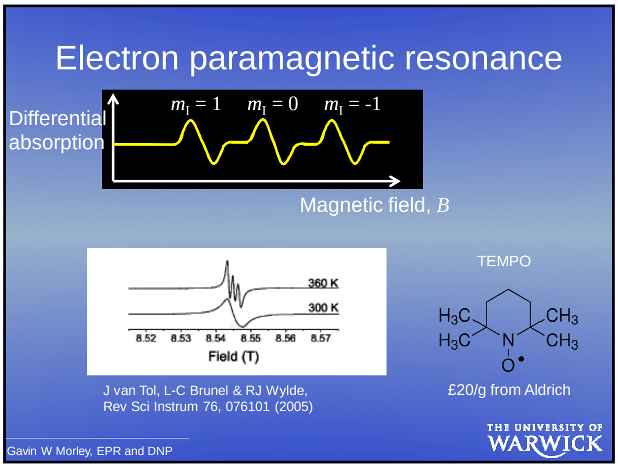
Electron paramagnetic resonance
Differential absorption
$m_I = 1$ $m_I = 0$ $m_I = -1$
Magnetic field, B
360 K
300 K
8.52 8.53 8.54 8.55 8.56 8.57
Field (T)
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)
TEMPO
H_3C CH_3 H_3C N CH_3 O•
£20/g from Aldrich
Gavin W Morley, EPR and DNP
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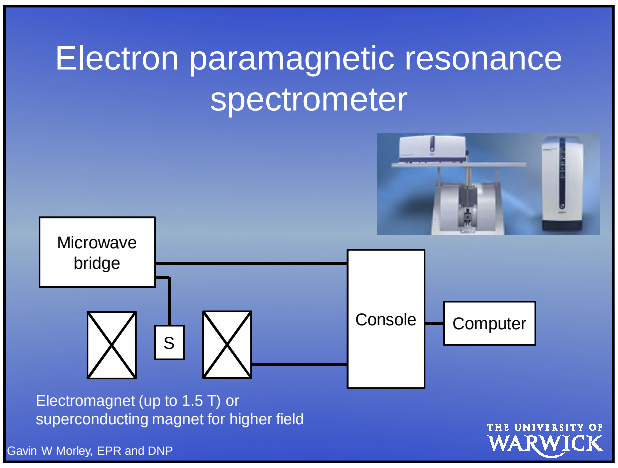
Electron paramagnetic resonance spectrometer
Microwave bridge
S
Console
Computer
Electromagnet (up to 1.5 T) or superconducting magnet for higher field
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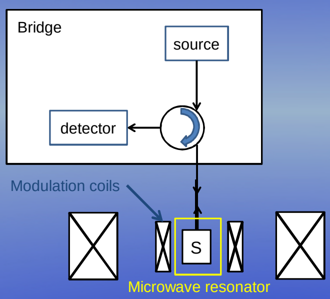
Electron paramagnetic resonance spectrometer

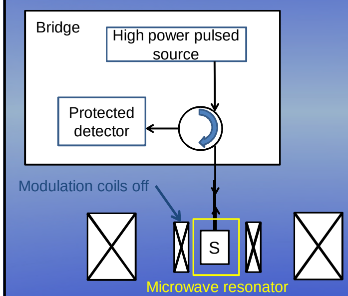


Electron paramagnetic resonance spectrometer

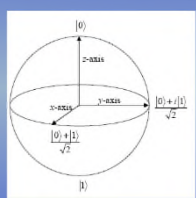
CW EPR so far…

Pulsed EPR next

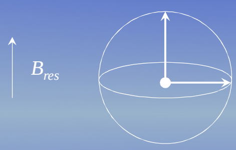
Pulsed electron paramagnetic resonance spectrometer



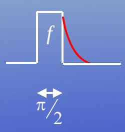
Pulsed electron paramagnetic resonance



Pulsed electron paramagnetic resonance



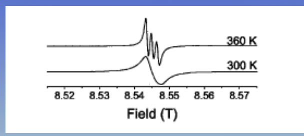
resonance condition
$g\ \mu_B\ B_{res} = h\ f$



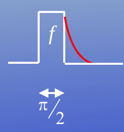
Polarize (thermalise) on timescale T_1

Free induction decay (FID) on timescale T_2^*

Pulsed EPR



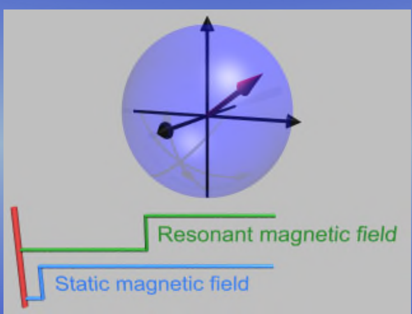
J van Tol, L-C Brunel & RJ Wylde, Rev Sci Instrum 76, 076101 (2005)



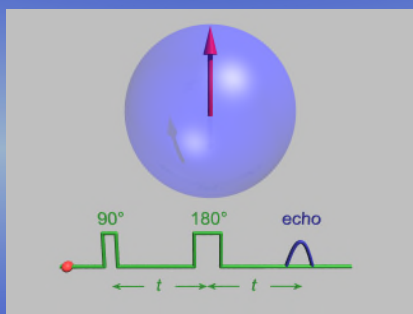
~100 MHz width
Pulse width < 500 MHz
Resonator ringing → deadtime
Short T_2 and T_2^* compared to NMR

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

Rotating frame

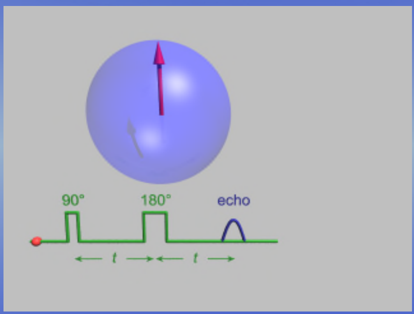


Spin echo



In rotating frame

Spin echo decay



Erwin L Hahn (born 1921)

Photo: AIP Emilio Segre Visual Archives, Stephen Jacobs Collection

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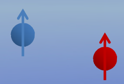
Pulsed EPR

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

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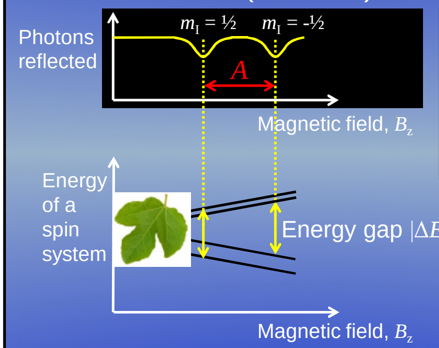
Electron nuclear double resonance (ENDOR)



S = ½
$m_s = \pm½$

I = ½
$m_I = \pm½\ (= m)$

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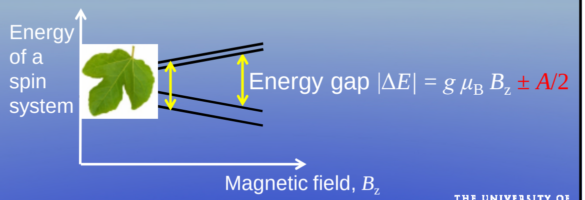
Electron nuclear double resonance (ENDOR)

Why do ENDOR instead of NMR?

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



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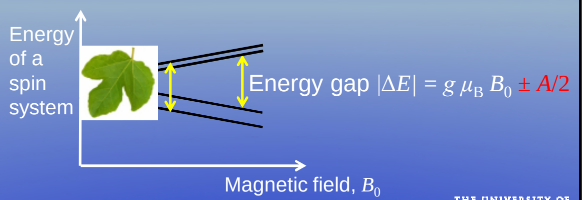
Electron nuclear double resonance (ENDOR)

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



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ENDOR for quantum computing

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

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Spin qubits in silicon

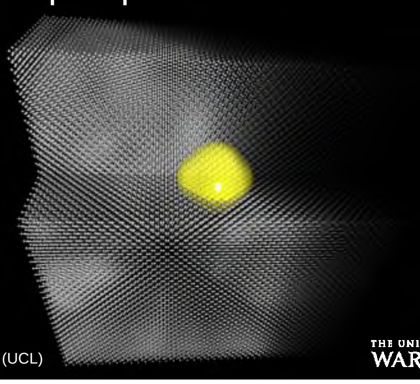

Image by
Manuel Vögtli (UCL)

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Other EPR applications

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

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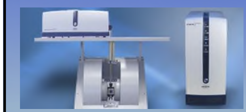
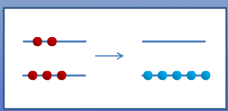
Overview

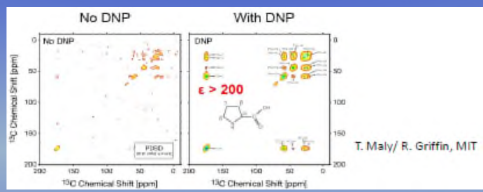


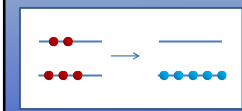
Electron paramagnetic resonance
- What it is
- Why it's useful



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

Dynamic nuclear polarization (DNP)





Dynamic nuclear polarization
- More signal

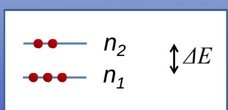
Dynamic nuclear polarization (DNP)

Thermal (Boltzmann) equilibrium:

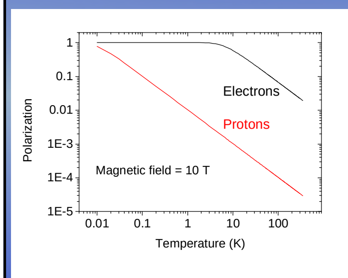
$$\frac{n_2}{n_1} = e^{-\frac{\Delta E}{k_B T}}$$

Define polarization as:

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



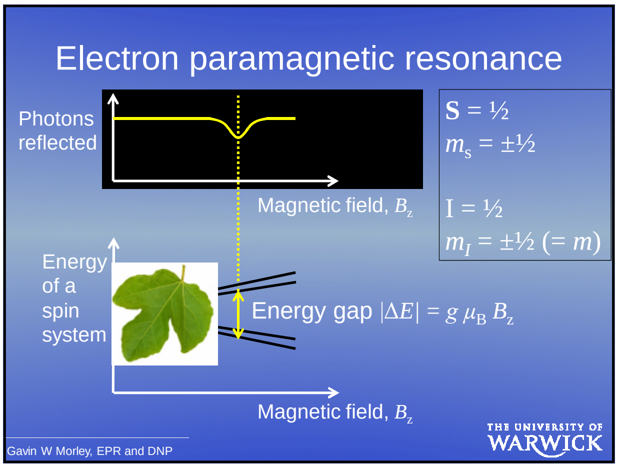
Dynamic nuclear polarization (DNP)



Boltzmann polarization:

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

So transfer electronic polarization to nuclei


Electron paramagnetic resonance
Photons reflected
Magnetic field, B_z
S = ½
$m_s = \pm½$
I = ½
$m_I = \pm½ \ (= m)$
Energy of a spin system
Energy gap $|\Delta E| = g\,\mu_B\,B_z$
Magnetic field, B_z
Gavin W Morley, EPR and DNP
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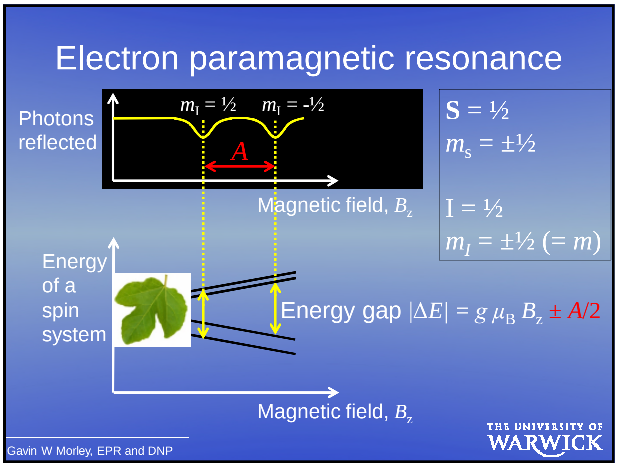
Electron paramagnetic resonance
Photons reflected
$m_I = ½$
$m_I = -½$
A
Magnetic field, B_z
S = ½
$m_s = \pm½$
I = ½
$m_I = \pm½ \ (= m)$
Energy of a spin system
Energy gap $|\Delta E| = g\,\mu_B\,B_z \pm A/2$
Magnetic field, B_z
Gavin W Morley, EPR and DNP
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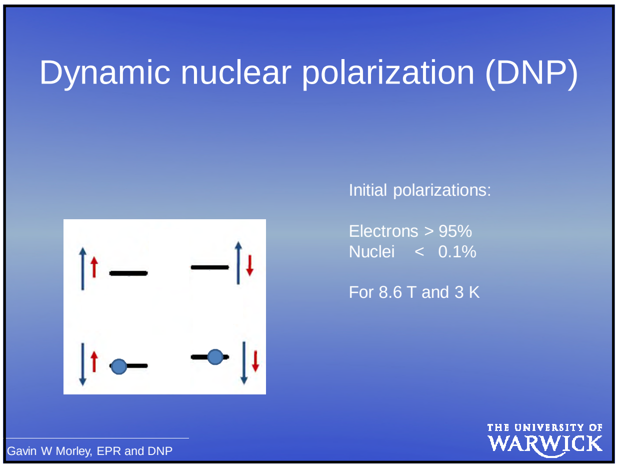
Dynamic nuclear polarization (DNP)
Initial polarizations:
Electrons > 95%
Nuclei < 0.1%
For 8.6 T and 3 K
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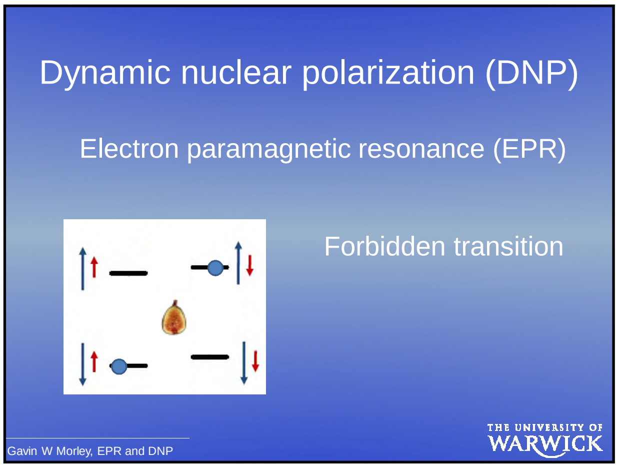
Dynamic nuclear polarization (DNP)
Electron paramagnetic resonance (EPR)
Forbidden transition
Gavin W Morley, EPR and DNP
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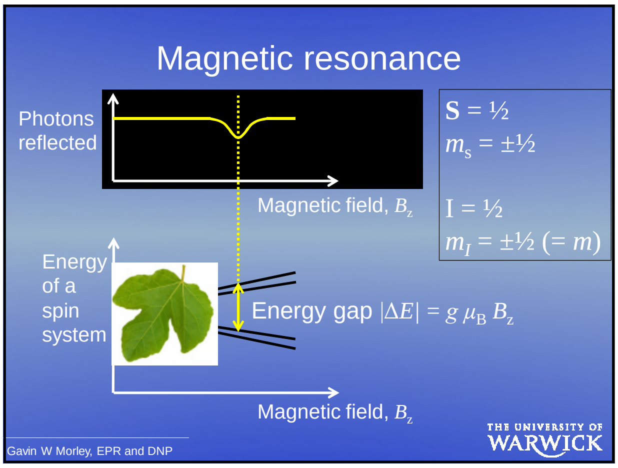
Magnetic resonance
Photons reflected
S = ½
m_s = ±½
I = ½
m_I = ±½ (= m)
Magnetic field, B_z
Energy of a spin system
Energy gap |ΔE| = g μ_B B_z
Magnetic field, B_z
Gavin W Morley, EPR and DNP
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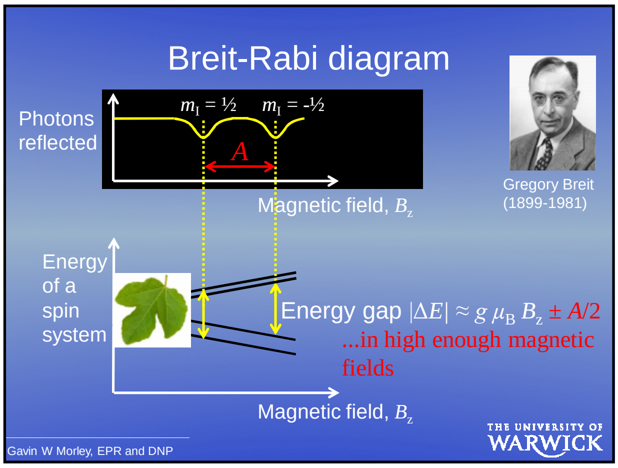
Breit-Rabi diagram
Photons reflected
m_I = ½
m_I = -½
A
Magnetic field, B_z
Gregory Breit (1899-1981)
Energy of a spin system
Energy gap |ΔE| ≈ g μ_B B_z ± A/2
...in high enough magnetic fields
Magnetic field, B_z
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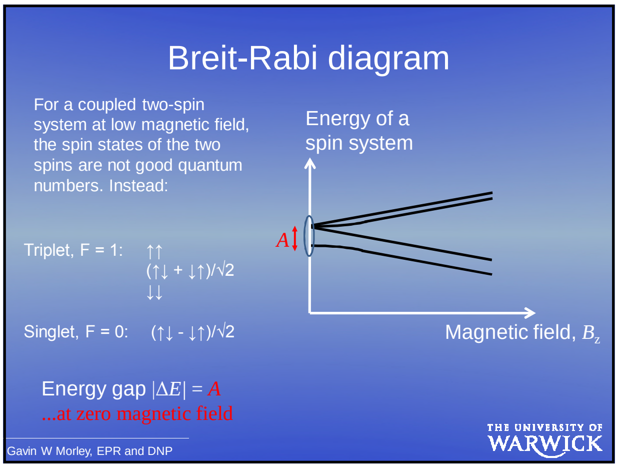
Breit-Rabi diagram
For a coupled two-spin system at low magnetic field, the spin states of the two spins are not good quantum numbers. Instead:
Triplet, F = 1: ↑↑
(↑↓ + ↓↑)/√2
↓↓
Singlet, F = 0: (↑↓ - ↓↑)/√2
Energy of a spin system
A
Magnetic field, B_z
Energy gap |ΔE| = A
...at zero magnetic field
Gavin W Morley, EPR and DNP
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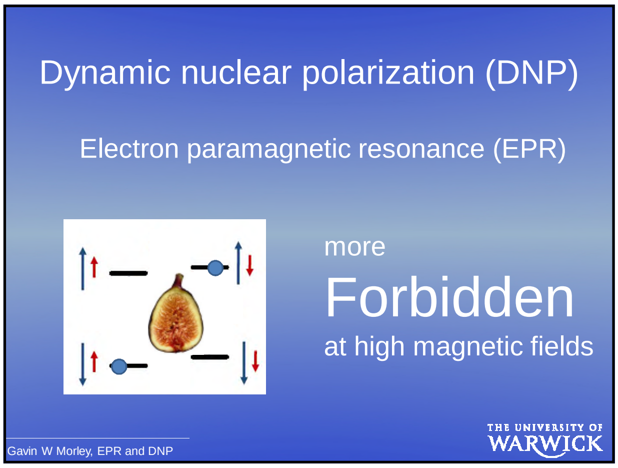
Dynamic nuclear polarization (DNP)
Electron paramagnetic resonance (EPR)
more
Forbidden
at high magnetic fields
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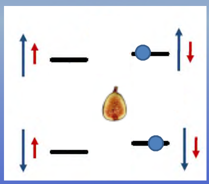
Dynamic nuclear polarization (DNP)

Solid effect DNP



also gets weaker at high magnetic fields

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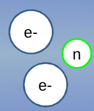
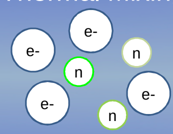
Dynamic nuclear polarization (DNP)

Cross effect



Thermal Mixing



also get weaker at high magnetic fields

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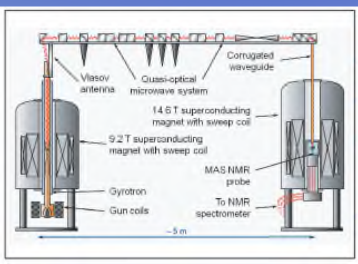
Dynamic nuclear polarization (DNP)



- Varian NMR console for NMR at 285 & 600 MHz
- Fukui gyrotron source for 185 and 395 GHz µwaves
- Thomas Keating and Uni. of St Andrews quasi optics
- Doty cryo-MAS probe with microwave mirrors for MAS at temperatures ~ 90 K and above
- Varian/Magnex 14.6 T (620 NMR) super-conducting magnet with 500 mT SC sweep coil

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

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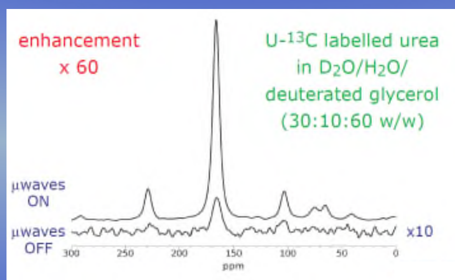
Dynamic nuclear polarization (DNP)



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

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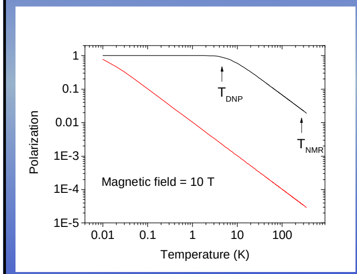
Dynamic nuclear polarization

Temperature jump



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

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

Gavin W Morley, EPR and DNP

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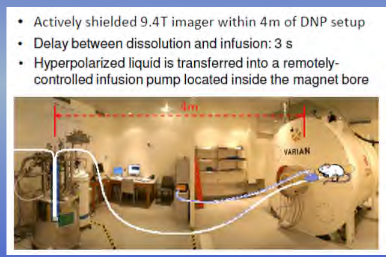
Dynamic nuclear polarization

Temperature jump with dissolution



Arnaud Comment and Rolf Gruetter, Lausanne

Gavin W Morley, EPR and DNP

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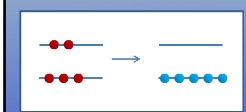
Conclusion

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



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

Gavin W Morley, EPR and DNP

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