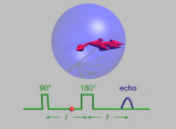


Electron Paramagnetic Resonance and Dynamic Nuclear Polarisation

CH916

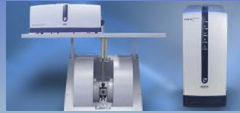


Gavin W Morley,
Department of Physics,
University of Warwick

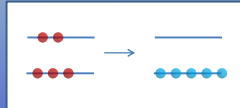
Gavin W Morley, EPR and DNP

1

Overview



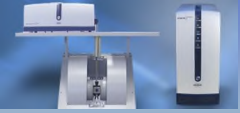
- Electron paramagnetic resonance
 - What it is
 - Why it's useful
- Dynamic nuclear polarization
 - Why it's useful
 - What it is



Gavin W Morley, EPR and DNP

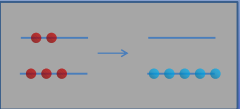
2

Overview



- Electron paramagnetic resonance
 - What it is
 - Why it's useful
- Dynamic nuclear polarization
 - Why it's useful
 - What it is

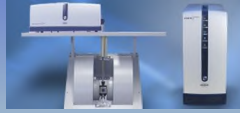
What does an EPR spectrum look like?
What is the resonant frequency for EPR?
Which things have an EPR signal?



Gavin W Morley, EPR and DNP

3

Overview



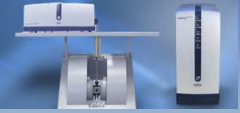
- Electron paramagnetic resonance
 - What it is

...NMR for electrons


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4

Electron paramagnetic resonance (EPR)




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




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5

Magnetism

Paramagnetism: follow 

Diamagnetism: oppose 

Ferromagnetism: ignore

Electron spins tend to: 

...an applied magnetic field

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6

Magnetic moments and magnetic fields

From Steven Brown's NMR lecture:

$$\text{Energy} = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z = -m\hbar\gamma B_z$$

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})

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Magnetic resonance


An isolated spin $I = 1/2$ has $m = \pm 1/2$


 Isidor Isaac Rabi (1898 – 1988)

Gavin W Morley, EPR and DNP

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Magnetic resonance


 Isidor Isaac Rabi (1898 – 1988)

Gavin W Morley, EPR and DNP

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Magnetic resonance


 Isidor Isaac Rabi (1898 – 1988)

Gavin W Morley, EPR and DNP

10


Magnetic resonance


 Isidor Isaac Rabi (1898 – 1988)

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Magnetic resonance


 Isidor Isaac Rabi (1898 – 1988)

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Magnetic resonance

Photons reflected

Magnetic field, B_z

Energy of a spin $S = 1/2$

Magnetic field, B_z

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

Pieter Zeeman (1865 - 1943)

Gavin W Morley, EPR and DNP

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Magnetic resonance condition

Photons reflected

Magnetic field, B_z

Energy of a spin $S = 1/2$

Magnetic field, B_z

Energy gap $|\Delta E| = g \mu_B B_z = h\nu_{res} = \hbar\omega_{res}$

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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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15

Electron paramagnetic resonance

Photons reflected

Magnetic field, B_z

Energy of a spin system

Magnetic field, B_z

Energy gap $|\Delta E| = g \mu_B B_z$

$S = 1/2$
 $m_s = \pm 1/2$

$I = 1/2$
 $m_I = \pm 1/2 (= m)$

Gavin W Morley, EPR and DNP

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Electron paramagnetic resonance

Photons reflected

Magnetic field, B_z

Energy of a spin system

Magnetic field, B_z

Energy gap $|\Delta E| = g \mu_B B_z$

$S = 1/2$
 $m_s = \pm 1/2$

$I = 1/2$
 $m_I = \pm 1/2 (= m)$

Gavin W Morley, EPR and DNP

17

Electron paramagnetic resonance

Photons reflected

Magnetic field, B_z

Energy of a spin system

Magnetic field, B_z

Energy gap $|\Delta E| = g \mu_B B_z \pm A/2$

A is the HYPERFINE COUPLING

$S = 1/2$
 $m_s = \pm 1/2$

$I = 1/2$
 $m_I = \pm 1/2 (= m)$

Gavin W Morley, EPR and DNP

18

Electron paramagnetic resonance

Photons reflected

Magnetic field, B_z

Stable free radicals:
BDPA
Nitroxides
DPPH

360 K

Field (T)

J van Tol, L-C Brunel & R.J Wylyde,
Rev Sci Instrum 76, 076101 (2005)

TEMPO

CN(C)(C)C1CC(C)CC1O

£20/g from Aldrich

Gavin W Morley, EPR and DNP

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Electron paramagnetic resonance

Photons absorbed

Magnetic field, B_z

360 K

Field (T)

J van Tol, L-C Brunel & R.J Wylyde,
Rev Sci Instrum 76, 076101 (2005)

TEMPO

CN(C)(C)C1CC(C)CC1O

£20/g from Aldrich

Gavin W Morley, EPR and DNP

20

Electron paramagnetic resonance

Photons absorbed

Magnetic field, B_z

360 K

Field (T)

J van Tol, L-C Brunel & R.J Wylyde,
Rev Sci Instrum 76, 076101 (2005)

TEMPO

CN(C)(C)C1CC(C)CC1O

£20/g from Aldrich

Gavin W Morley, EPR and DNP

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Electron paramagnetic resonance

Photons absorbed

Magnetic field, B

Magnetic field modulation
(~10 to 100 kHz)

Advantage:
noise only at
modulation
frequency

Differential absorption

Gavin W Morley, EPR and DNP

22

Electron paramagnetic resonance

Differential absorption

Magnetic field, B

360 K

Field (T)

J van Tol, L-C Brunel & R.J Wylyde,
Rev Sci Instrum 76, 076101 (2005)

TEMPO

CN(C)(C)C1CC(C)CC1O

£20/g from Aldrich

Gavin W Morley, EPR and DNP

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Electron paramagnetic resonance

Differential absorption

Magnetic field, B

360 K
300 K

Field (T)

J van Tol, L-C Brunel & R.J Wylyde,
Rev Sci Instrum 76, 076101 (2005)

TEMPO

CN(C)(C)C1CC(C)CC1O

£20/g from Aldrich

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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

Bridge

source

detector

Modulation coils

S

Microwave resonator

Gavin W Morley, EPR and DNP

26

Electron paramagnetic resonance spectrometer

Bridge

source

detector

Modulation coils

S

Microwave resonator

Gavin W Morley, EPR and DNP

27

Electron paramagnetic resonance spectrometer

Bridge

source

detector

Modulation coils

S

Microwave resonator

Gavin W Morley, EPR and DNP

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Electron paramagnetic resonance spectrometer

CW EPR so far...

Pulsed EPR next

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29

Pulsed electron paramagnetic resonance spectrometer

Bridge

High power pulsed source

Protected detector

Modulation coils off

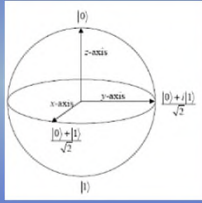
S

Microwave resonator

Gavin W Morley, EPR and DNP

30

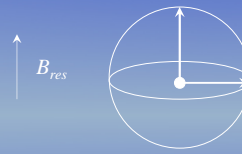
Pulsed electron paramagnetic resonance



Gavin W Morley, EPR and DNP

31

Pulsed electron paramagnetic resonance



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

Polarize (thermalize) on timescale T_1

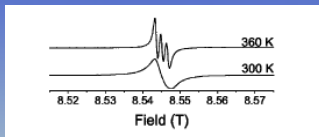


Free induction decay (FID) on timescale T_2^*

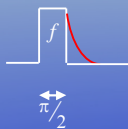
Gavin W Morley, EPR and DNP

32

Pulsed EPR



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



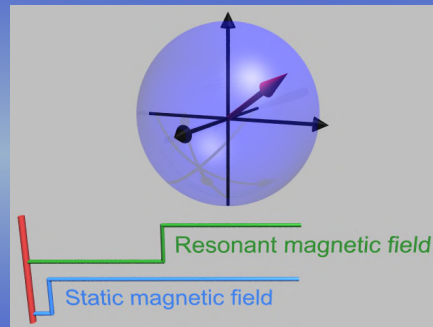
~100 MHz width
Pulse width < 500 MHz
Resonator ringing → deadtime
Short T_2 and T_2^* compared to NMR

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

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33

The rotating frame of reference

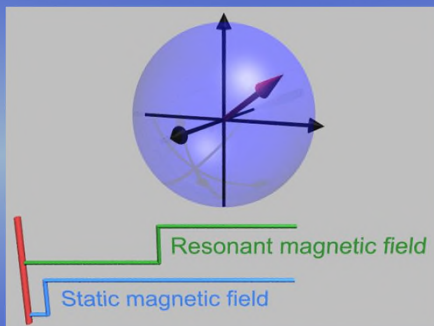


Larmor precession

Gavin W Morley, EPR and DNP

34

The rotating frame of reference

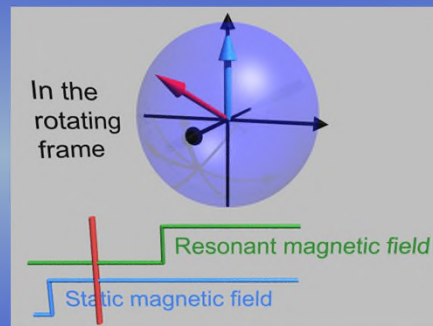


Larmor precession

Gavin W Morley, EPR and DNP

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The rotating frame of reference



In the rotating frame

Larmor precession

Gavin W Morley, EPR and DNP

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Rotating frame

Resonant magnetic field

Static magnetic field

Gavin W Morley, EPR and DNP

37

Spin echo

90° 180° echo

t t

In rotating frame

Gavin W Morley, EPR and DNP

38

Spin echo

90° 180° echo

t t

In rotating frame

Gavin W Morley, EPR and DNP

39

Spin echo decay

90° 180° echo

t t

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

Gavin W Morley, EPR and DNP

40

Spin echo decay

90° 180° echo

t t

Erwin L Hahn (1921-2016)
Photo: AIP Emilio Segre Visual Archives, Stephen Jacobs Collection

Gavin W Morley, EPR and DNP

41

Pulsed EPR

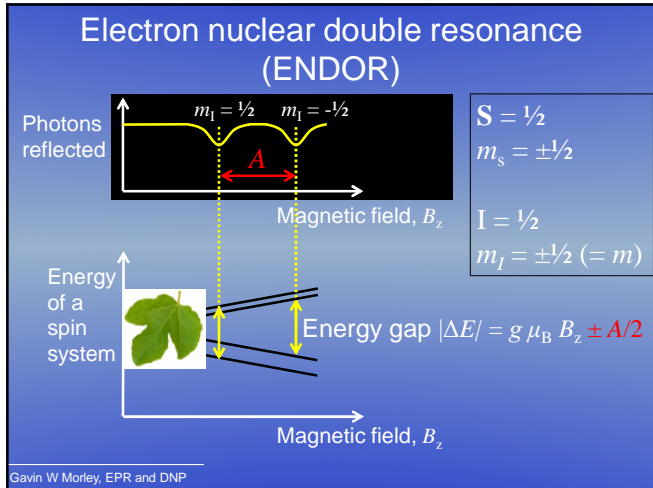
Double electron-electron resonance (DEER) allows distances between two electron spins in the range 2 to 6 nm to be measured (cf < 1 nm by NMR for two nuclear spins)

Dipolar coupling $\propto 1/r^3$

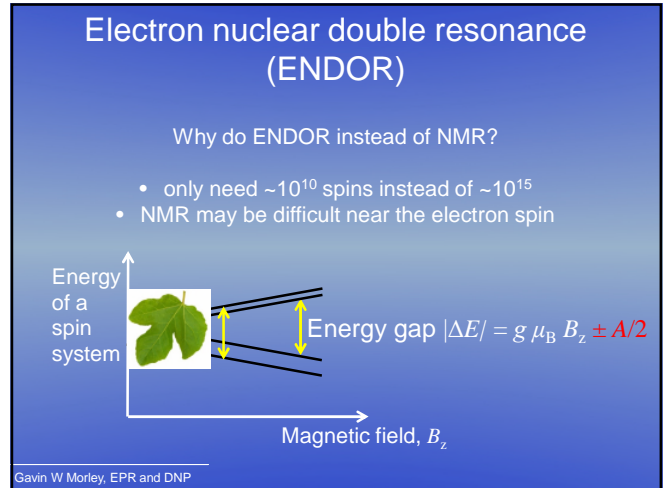
Site directed spin labelling with one or more TEMPO

Gavin W Morley, EPR and DNP

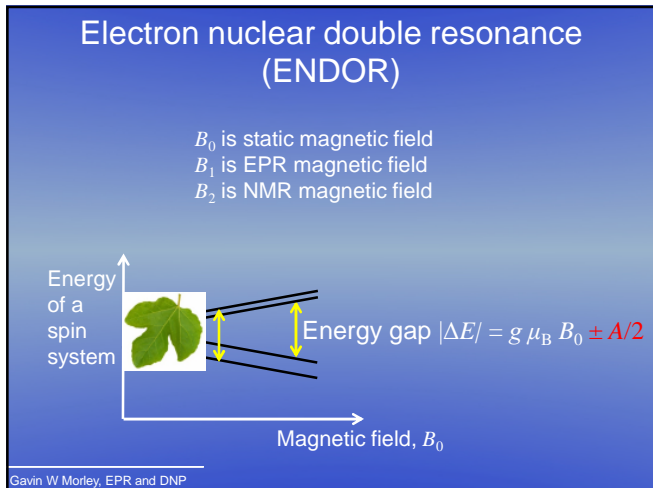
42



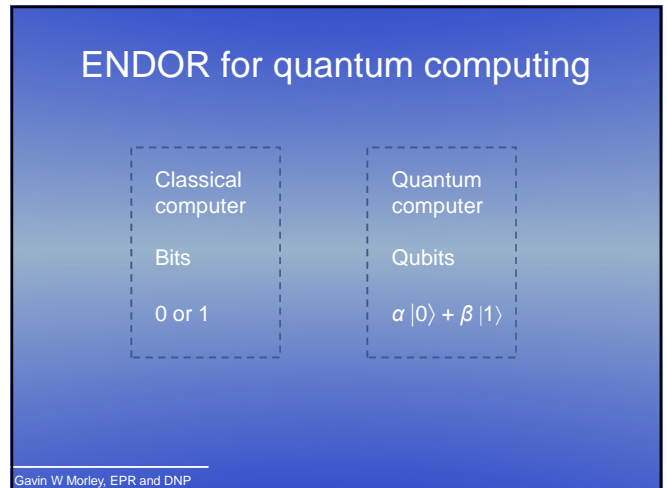
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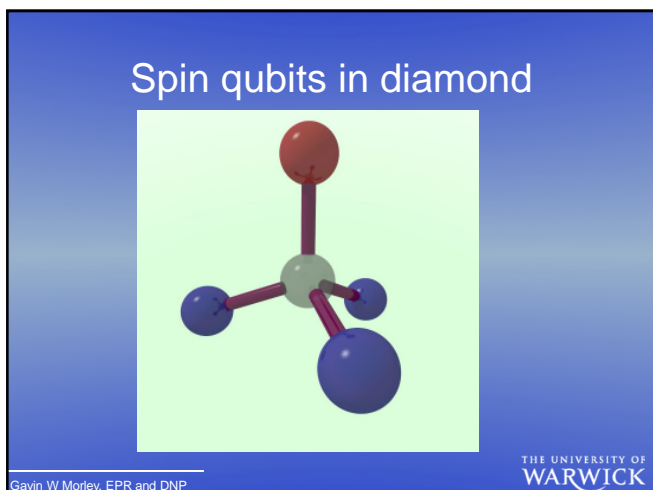
44



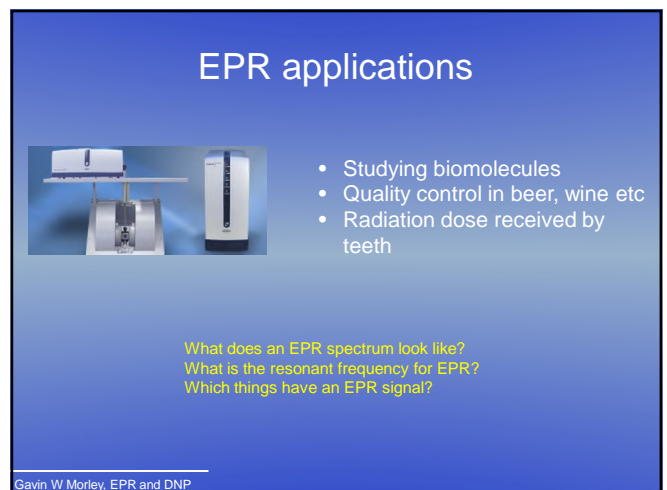
45



46

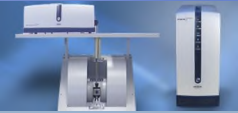


47



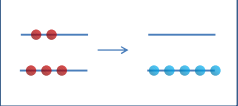
48

Overview



Electron paramagnetic resonance

- What it is
- Why it's useful



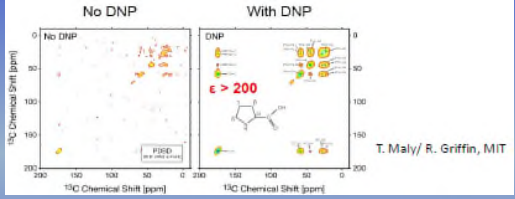
Dynamic nuclear polarization

- Why it's useful
- What it is

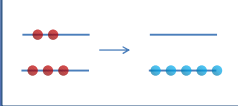
Gavin W Morley, EPR and DNP

49

Dynamic nuclear polarization (DNP)



T. Maly/ R. Griffin, MIT



Dynamic nuclear polarization

- More signal

Gavin W Morley, EPR and DNP

50

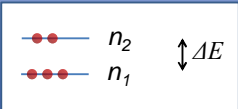
Dynamic nuclear polarization (DNP)

Thermal (Boltzmann) equilibrium:

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

Define polarization as:

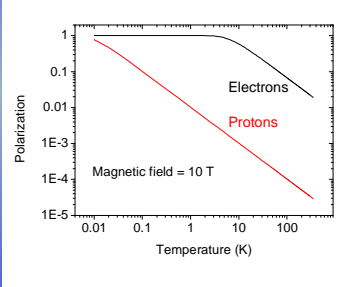
$$P = \frac{n_1 - n_2}{n_1 + n_2}$$



Gavin W Morley, EPR and DNP

51

Dynamic nuclear polarization (DNP)



Boltzmann polarization:

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

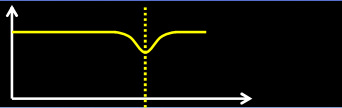
So transfer electronic polarization to nuclei

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52

Electron paramagnetic resonance


Photons reflected



$S = 1/2$
 $m_s = \pm 1/2$

$I = 1/2$
 $m_I = \pm 1/2 (= m)$

Energy of a spin system



Energy gap $|\Delta E| = g \mu_B B_z$

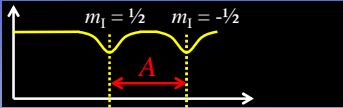
Magnetic field, B_z

Gavin W Morley, EPR and DNP

53

Electron paramagnetic resonance

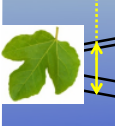
Photons reflected



$S = 1/2$
 $m_s = \pm 1/2$

$I = 1/2$
 $m_I = \pm 1/2 (= m)$

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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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)

Nuclear magnetic resonance (NMR)

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Dynamic nuclear polarization (DNP)

Electron paramagnetic resonance (EPR)

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57

Dynamic nuclear polarization (DNP)

Electron paramagnetic resonance (EPR)

Forbidden transition
→ Overhauser Effect

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58

Magnetic resonance

Photons reflected

Magnetic field, B_z

Energy of a spin system

Energy gap $|\Delta E| = g \mu_B B_z$

Magnetic field, B_z

$S = 1/2$
 $m_s = \pm 1/2$

$I = 1/2$
 $m_I = \pm 1/2 (= m)$

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59

Breit-Rabi diagram

Photons reflected

Magnetic field, B_z

Energy of a spin system

Energy gap $|\Delta E| \approx g \mu_B B_z \pm A/2$
...in high enough magnetic fields

Magnetic field, B_z

$m_I = 1/2$ $m_I = -1/2$

A

Gregory Breit (1899-1981)

Gavin W Morley, EPR and DNP

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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, $F = 1$: $\begin{matrix} \uparrow\uparrow \\ (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2} \\ \downarrow\downarrow \end{matrix}$

Singlet, $F = 0$: $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$

Energy gap $|\Delta E| = A$
...at zero magnetic field

Energy of a spin system

Magnetic field, B_z

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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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63

Dynamic nuclear polarization (DNP)

Solid effect DNP

also gets weaker at high magnetic fields

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64

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 μ waves
- 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)

Gavin W Morley, EPR and DNP

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Dynamic nuclear polarization (DNP)

enhancement x 60

U-¹³C labelled urea in D₂O/H₂O/deuterated glycerol (30:10:60 w/w)

μwaves ON

μwaves OFF

300 250 200 150 100 50 0 ppm

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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Solid-state DNP

Commercial solid-state DNP-NMR:
400-900 MHz NMR
200x signal enhancement -> 200² quicker scans

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68

Liquid-state DNP

Temperature jump

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

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

Magnetic field = 10 T

Gavin W Morley, EPR and DNP

69

Liquid-state DNP

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

Gavin W Morley, EPR and DNP

70

Parahydrogen-induced polarization (PHIP) for liquid-state NMR

SPIN ISOMERS OF MOLECULAR HYDROGEN

PROTON SPIN

COVALENT BOND

ORTHOHYDROGEN

PARAHYDROGEN

Hydrogen at low temperatures becomes almost pure parahydrogen

Image by Xaa (Jim Farris)

Gavin W Morley, EPR and DNP

71

Parahydrogen-induced polarization (PHIP) for liquid-state NMR

Molecule precursor

pH₂

Catalyst

Parahydrogenated molecule

Spin order transfer

X hyperpolarized molecule

Review: F. Reineri, E. Cavallari, C. Carrera & S. Aime, Magn. Reson. Mater. Phys., Biol. Med. **34**, 25 (2021).

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72

Parahydrogen-induced polarization (PHIP) for liquid-state NMR

1. A company (eg NVision) creates parahydrogen and ships it to users. It stays stable for months.
2. Polarization is transferred to a natural metabolite by catalytically adding parahydrogen to a precursor.
3. After purification, the hyperpolarized metabolite (eg pyruvate) is ready to be injected.
4. Do MRI to image the metabolism.



Gavin W Morley, EPR and DNP

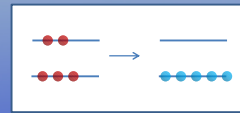
73

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

74