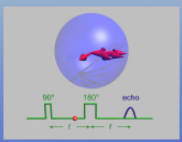
Electron Paramagnetic Resonance and Dynamic Nuclear Polarisation

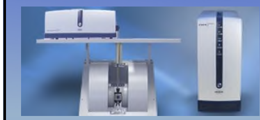
CH916



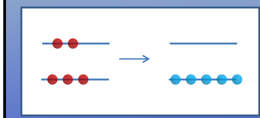
Gavin W Morley,
Department of Physics,
University of Warwick

1

Overview



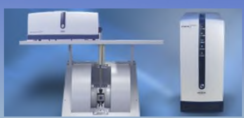
Electron paramagnetic resonance
- What it is
- Why it's useful



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

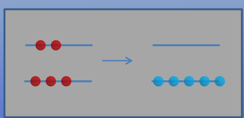
2

Overview



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

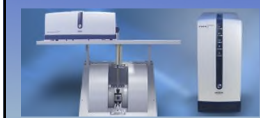
What does an EPR spectrum look like?
What is the resonant frequency for EPR?
Which things have an EPR signal?



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

3

Overview



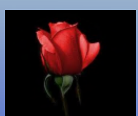
Electron paramagnetic resonance
- What it is

…NMR for electrons

4

Electron paramagnetic resonance (EPR)

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



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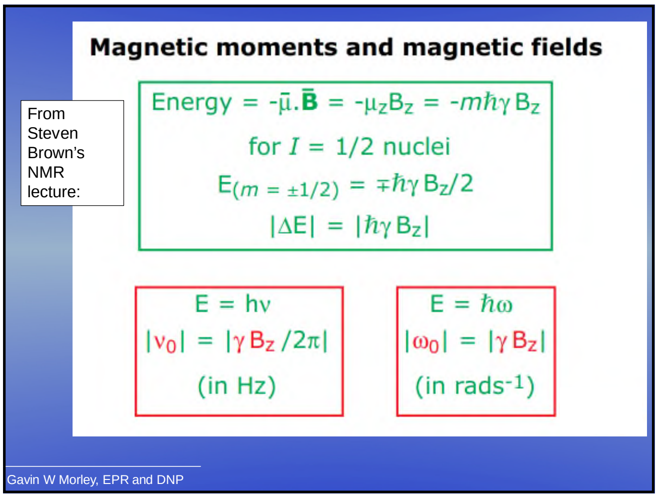
Magnetism

Electron spins tend to:

Paramagnetism:	follow
Diamagnetism:	oppose
Ferromagnetism:	ignore

…an applied magnetic field

6


Magnetic moments and magnetic fields
From Steven Brown's NMR lecture:
$\text{Energy} = -\bar{\mu}.\bar{\mathbf{B}} = -\mu_z B_z = -m\hbar\gamma B_z$
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})
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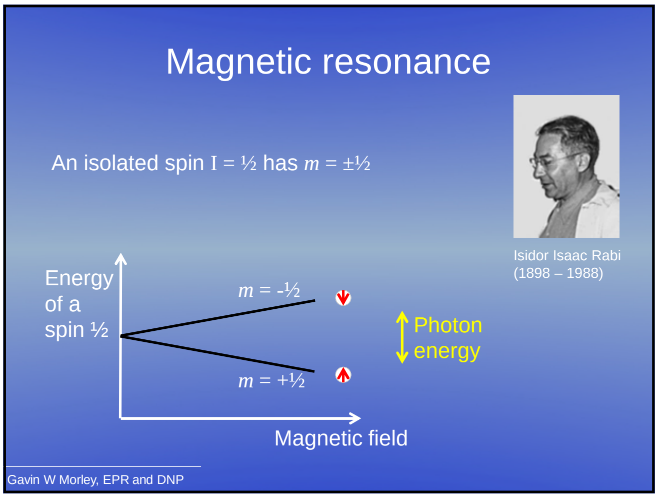
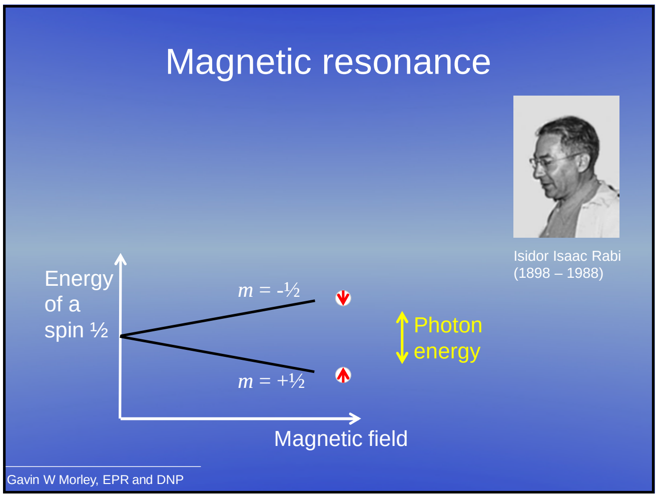
7


Magnetic resonance
An isolated spin I = ½ has m = ±½
Isidor Isaac Rabi (1898 – 1988)
Energy of a spin ½
m = -½
m = +½
Photon energy
Magnetic field
Gavin W Morley, EPR and DNP

8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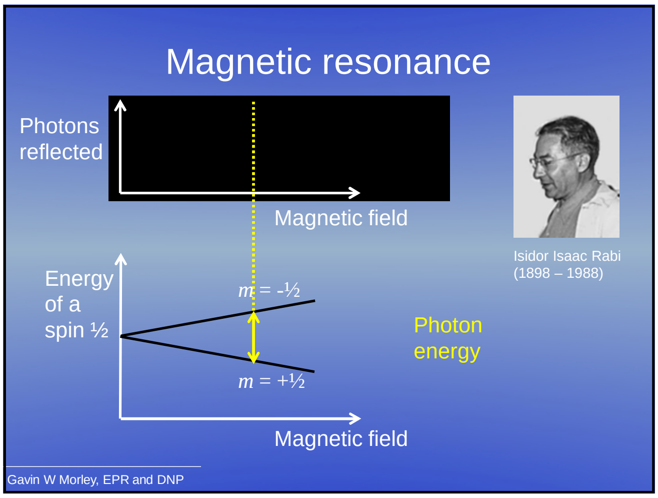
Gavin W Morley, EPR and DNP

9


Magnetic resonance
Photons reflected
Magnetic field
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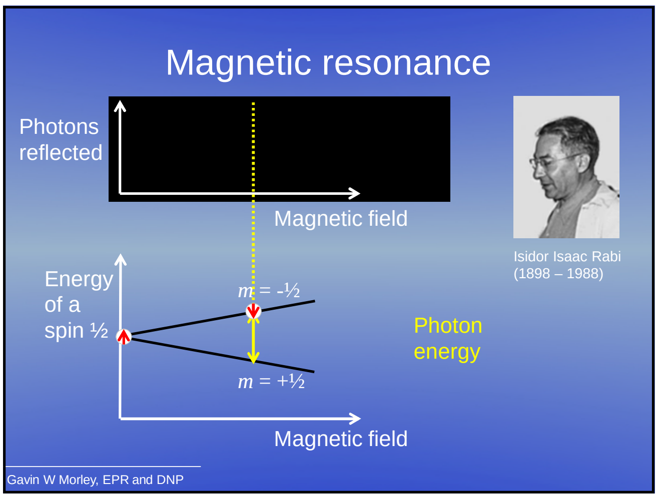
10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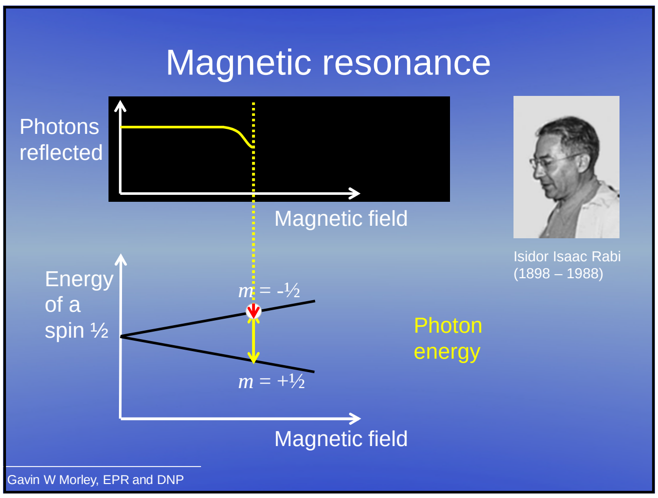
11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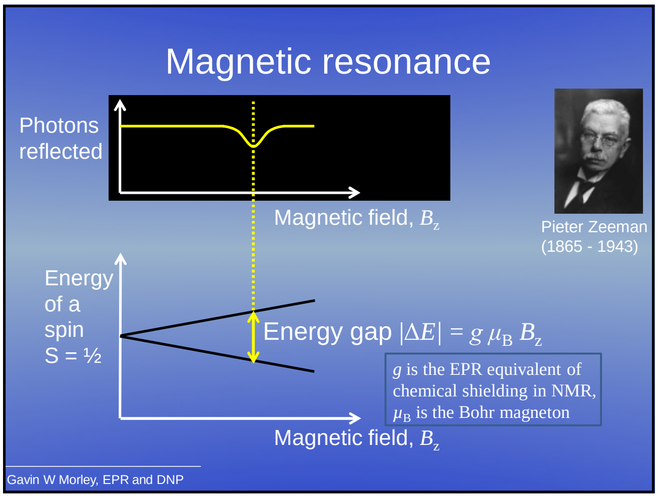
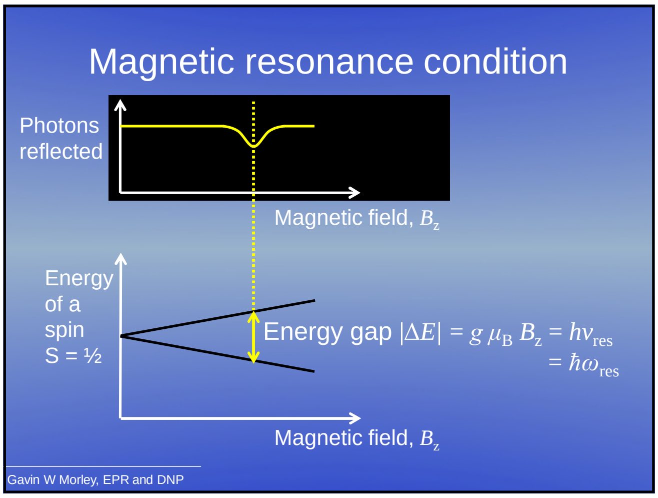
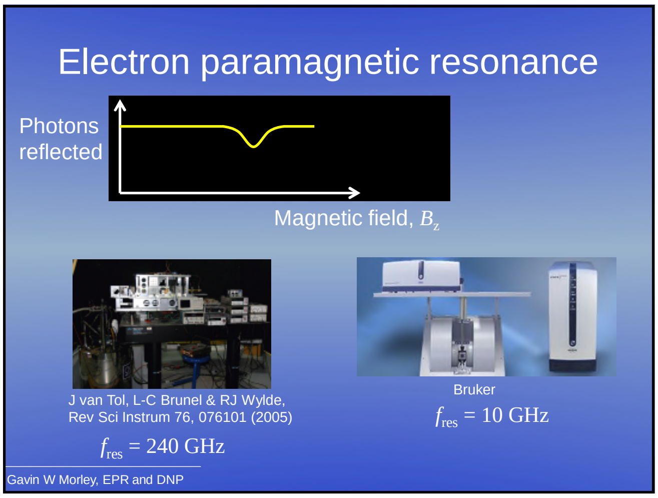
12



13



14



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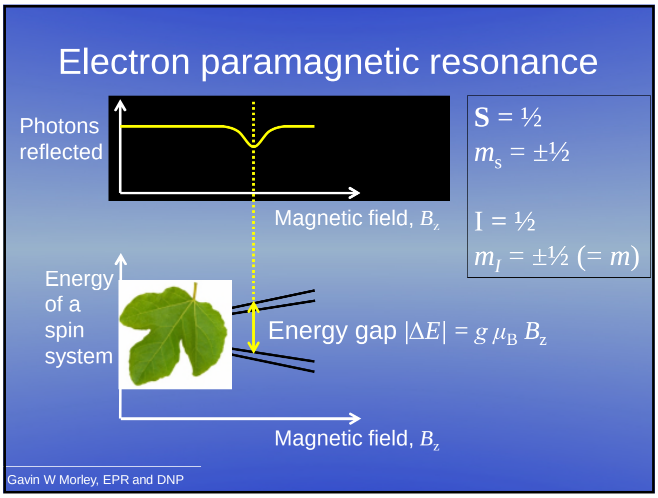

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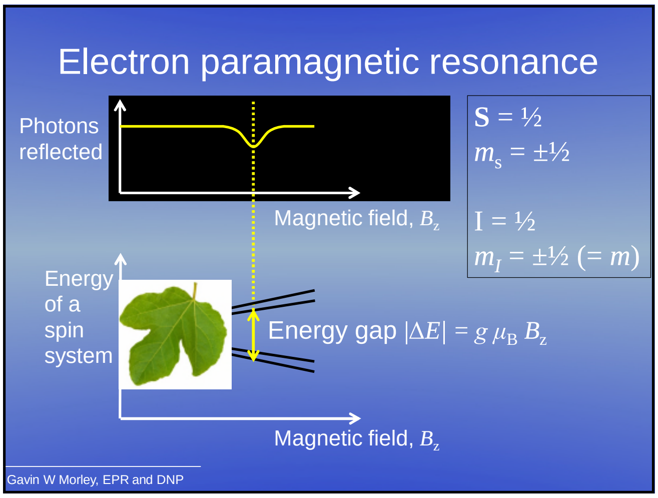
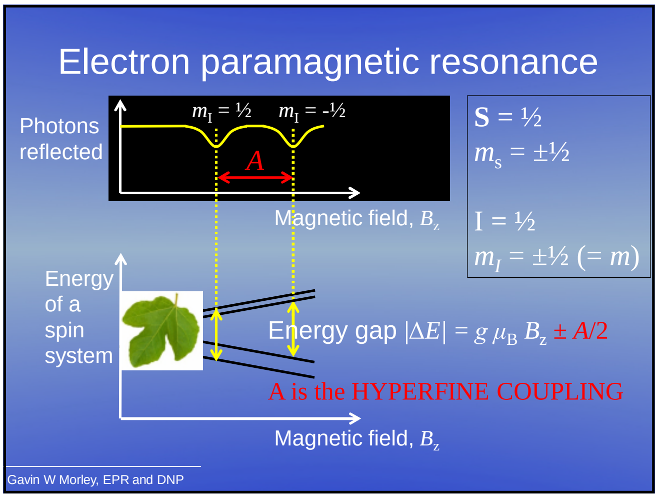
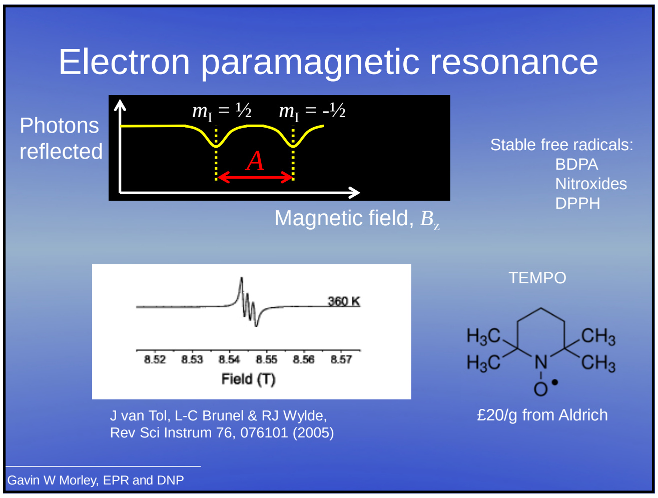


17



18



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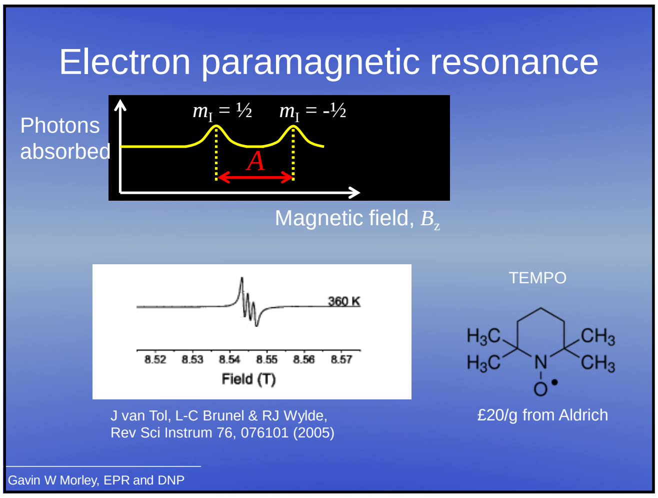

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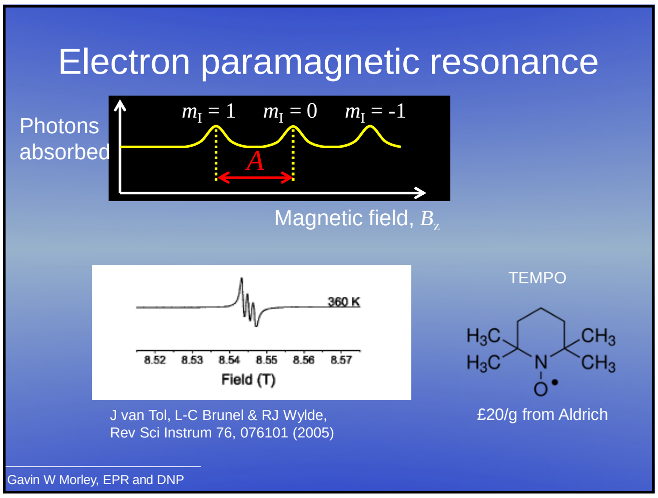

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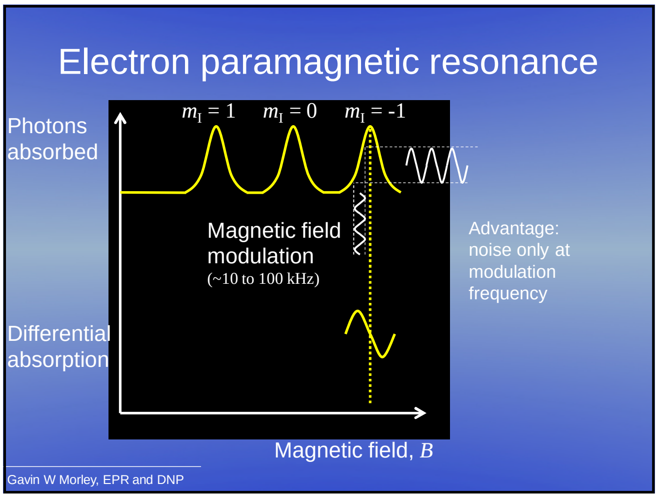

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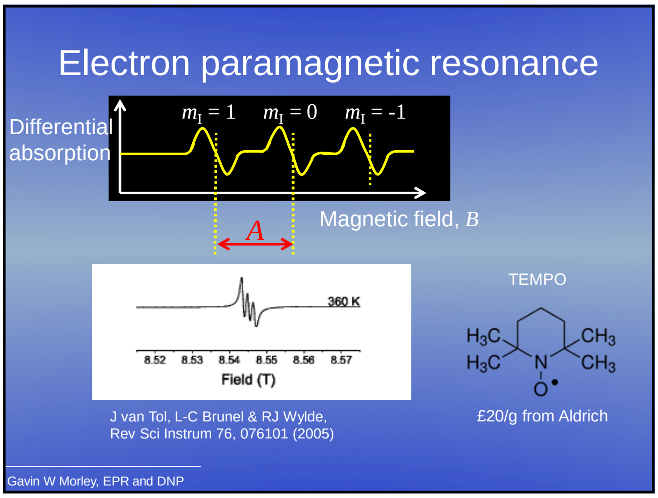

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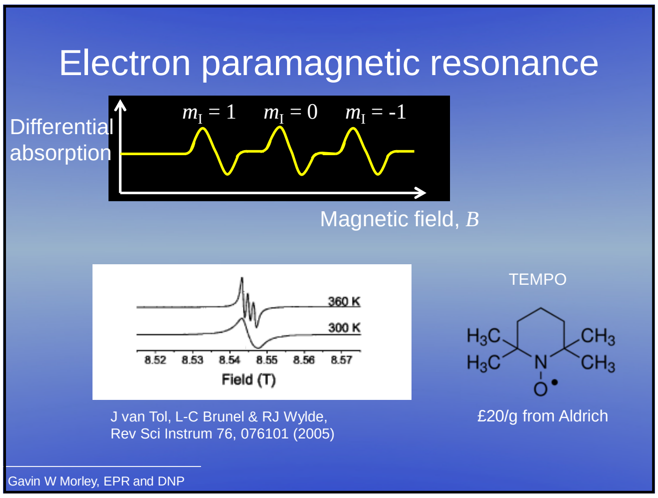
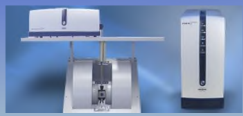
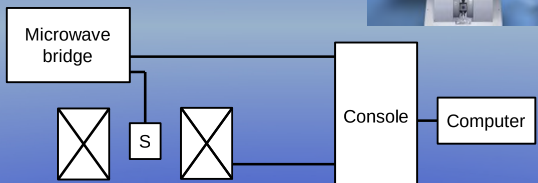


24

Electron paramagnetic resonance spectrometer





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

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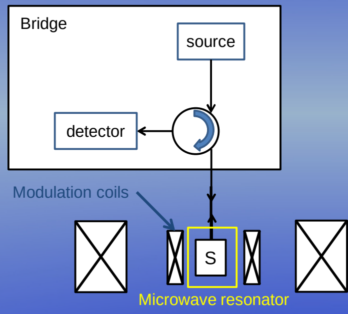
25

Electron paramagnetic resonance spectrometer



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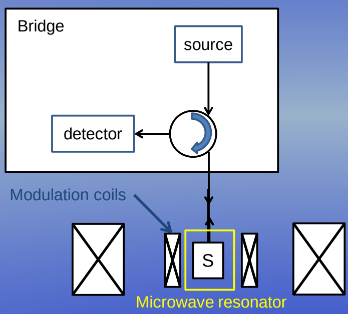
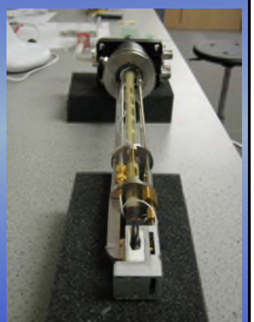
26

Electron paramagnetic resonance spectrometer





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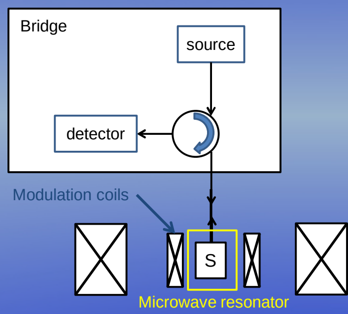
27

Electron paramagnetic resonance spectrometer



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Electron paramagnetic resonance spectrometer

CW EPR so far…

Pulsed EPR next

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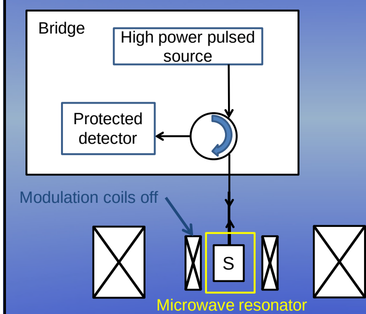
29

Pulsed electron paramagnetic resonance spectrometer



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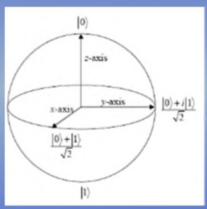
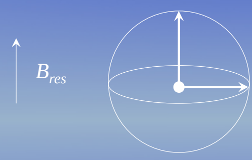
30

Pulsed electron paramagnetic resonance



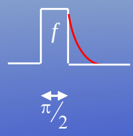
31

Pulsed electron paramagnetic resonance



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

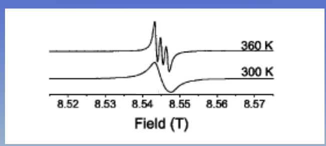
Polarize (thermalize) on timescale T_1



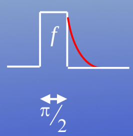
Free induction decay (FID) on timescale T_2^*

32

Pulsed EPR



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

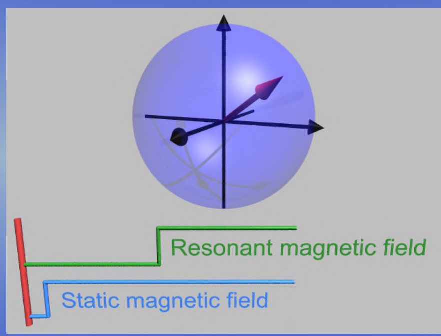


↔
~100 MHz width
Pulse width < 500 MHz
Resonator ringing → deadtime
Short T_2 and T_2^* compared to NMR

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

33

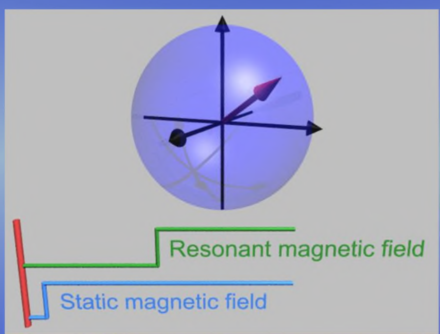
The rotating frame of reference



Larmor precession

34

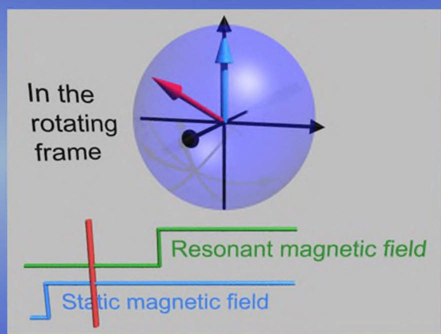
The rotating frame of reference



Larmor precession

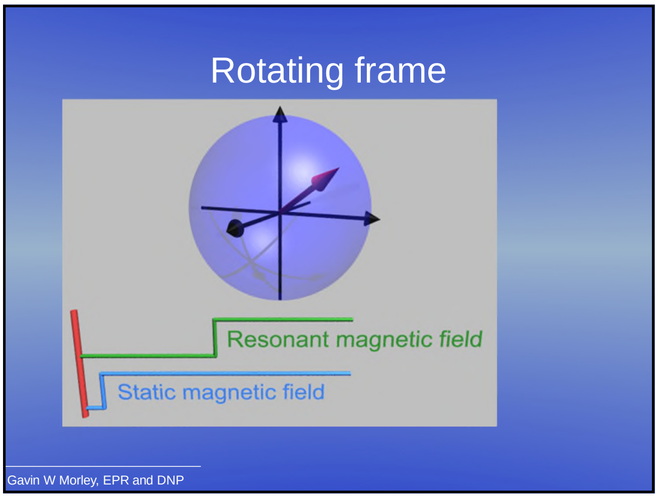
35

The rotating frame of reference

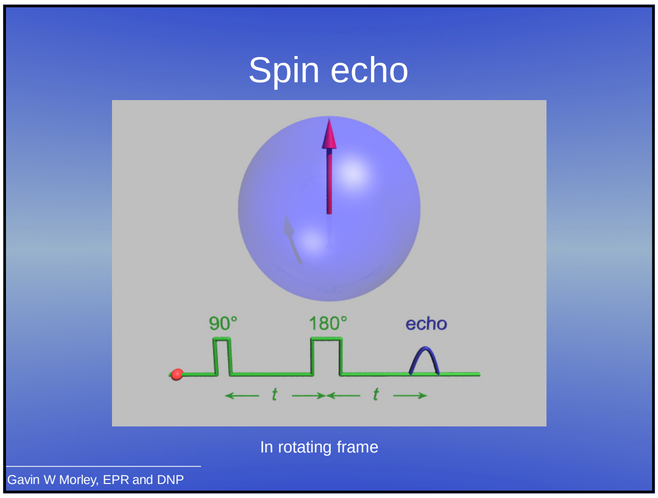


Larmor precession

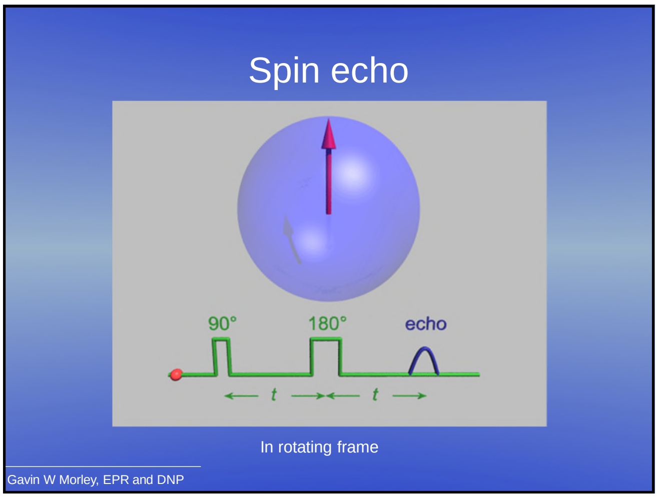
36



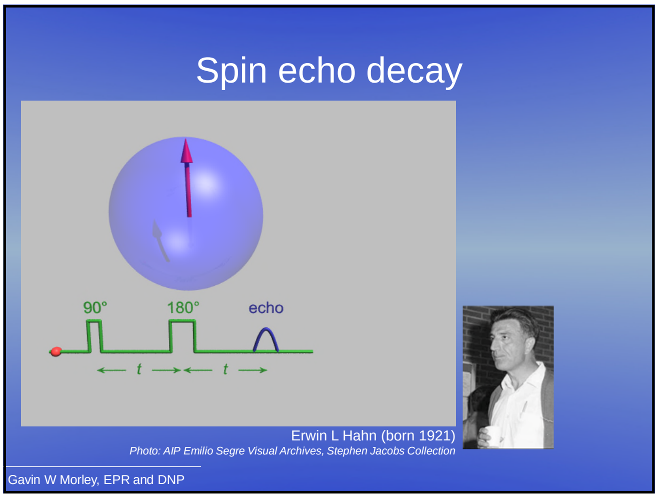
37



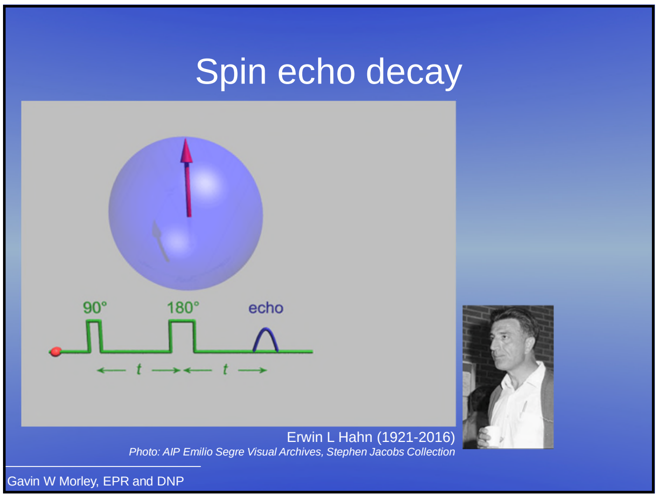
38



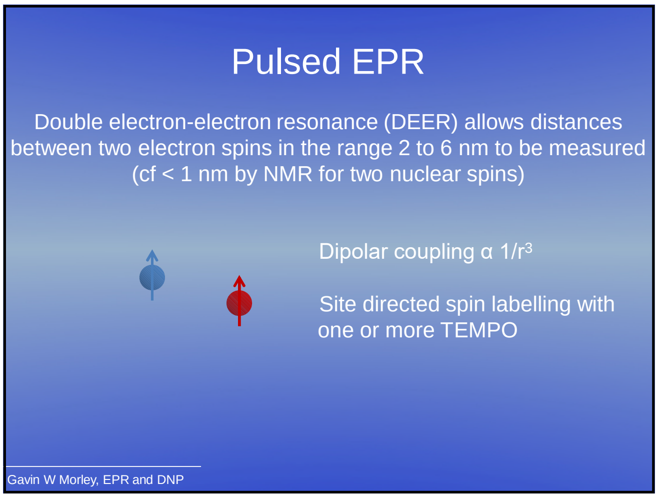
39



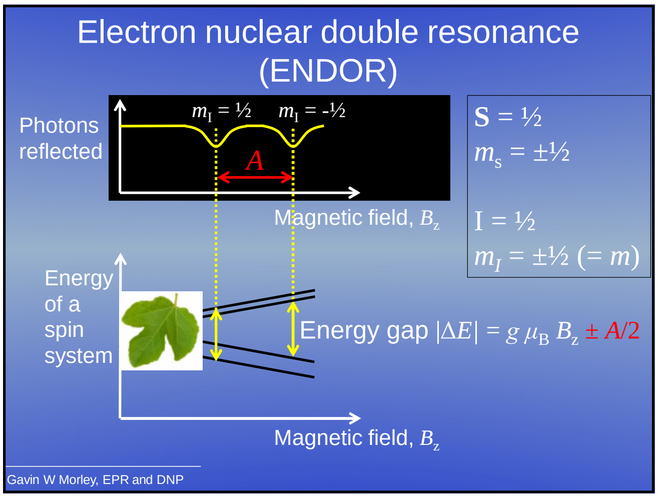
40



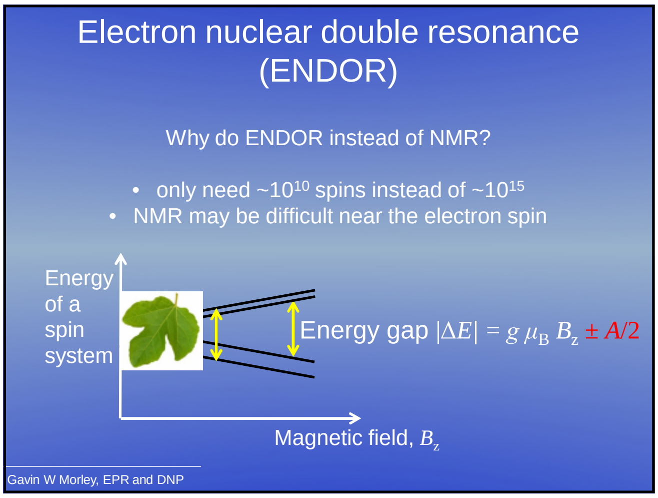
41



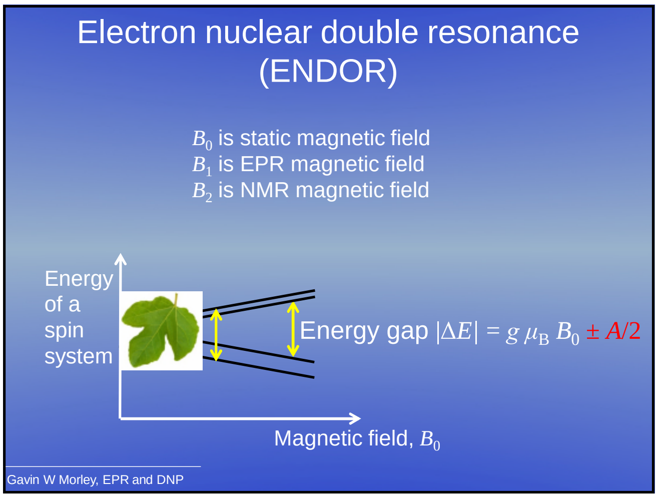
42



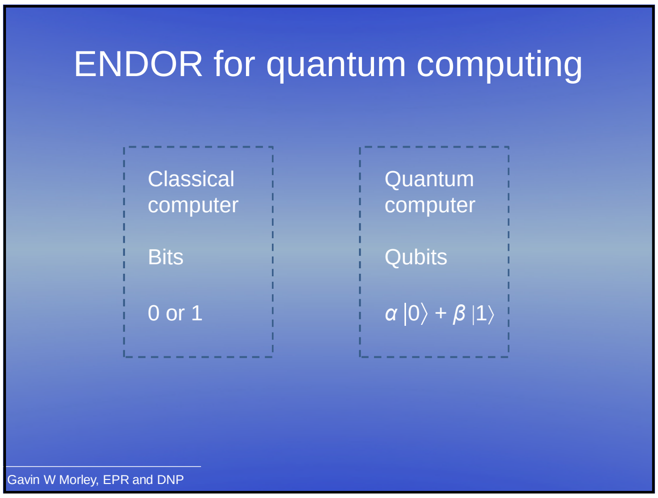
43



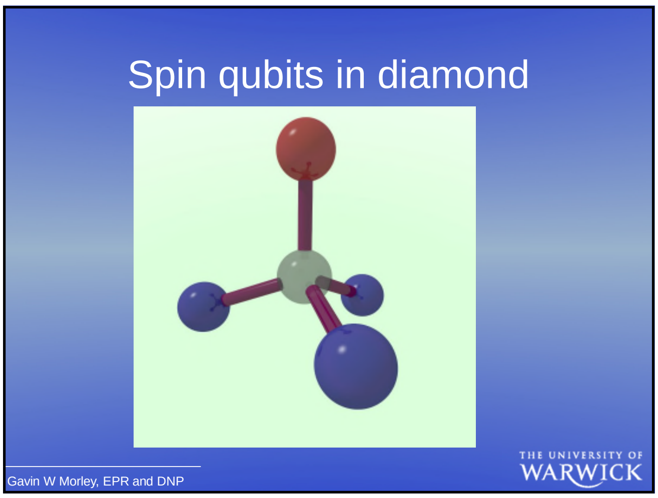
44



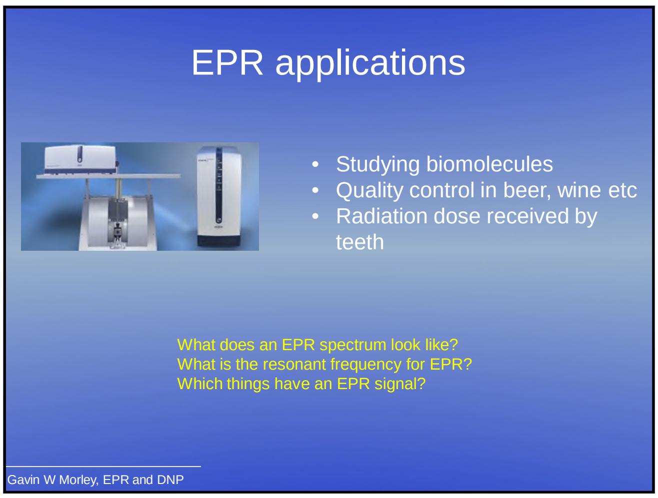
45



46



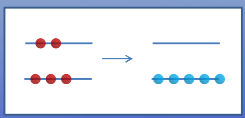
47



48

Overview

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



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

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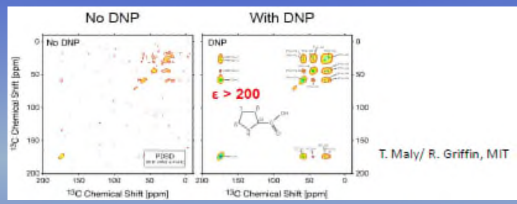
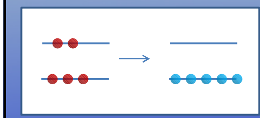
49

Dynamic nuclear polarization (DNP)





Dynamic nuclear polarization
- More signal

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50

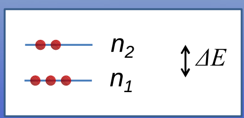
Dynamic nuclear polarization (DNP)

Thermal (Boltzmann) equilibrium:

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

Define polarization as:

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



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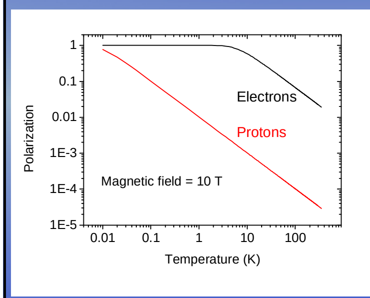
51

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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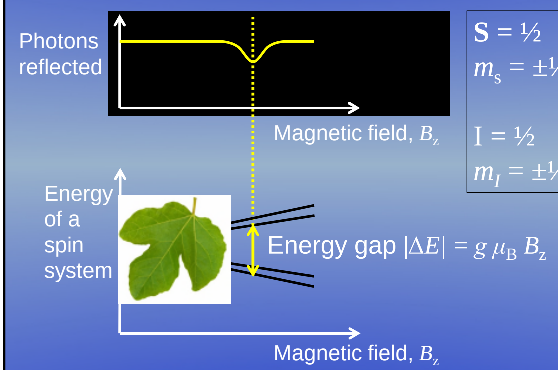
52

Electron paramagnetic resonance



$\mathbf{S} = ½$
$m_s = ±½$

$I = ½$
$m_I = ±½ \; (= m)$

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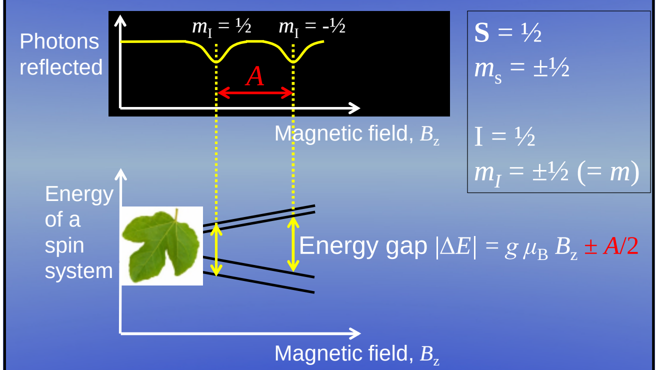
53

Electron paramagnetic resonance



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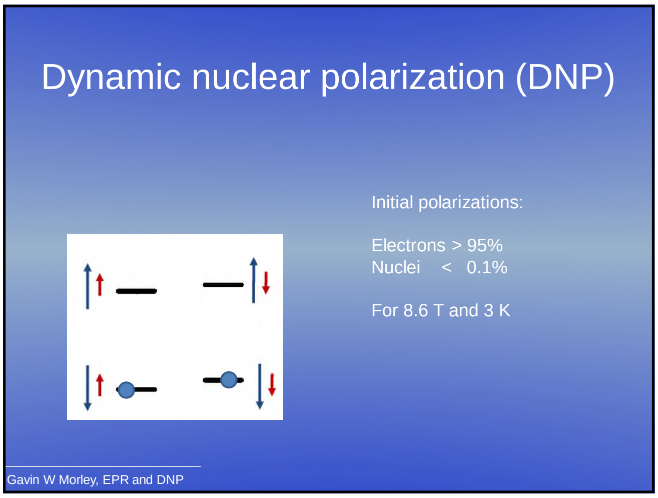
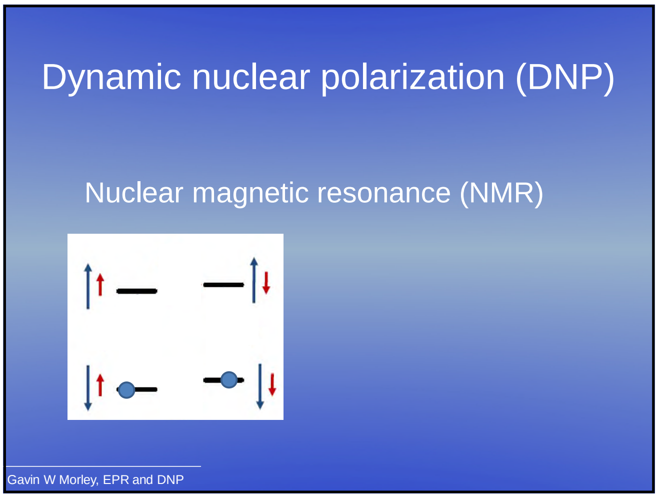
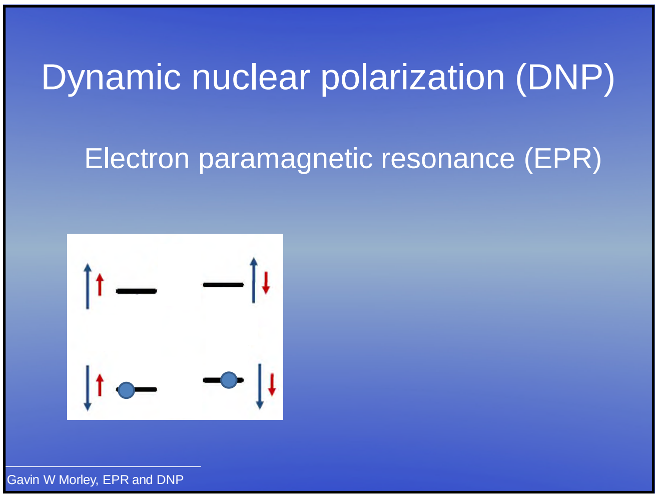
54



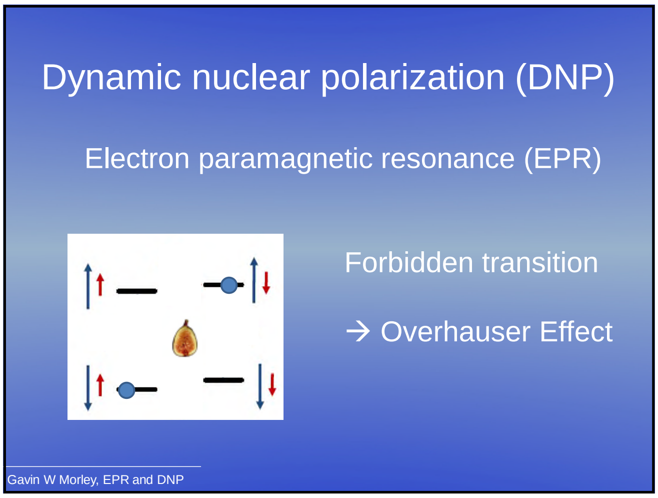
55



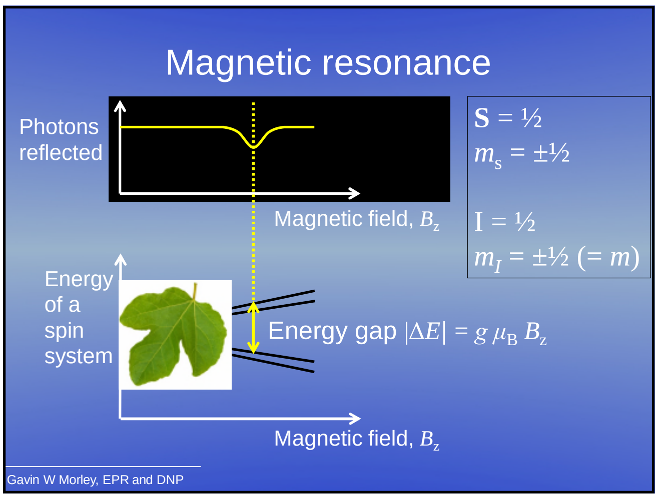
56



57



58



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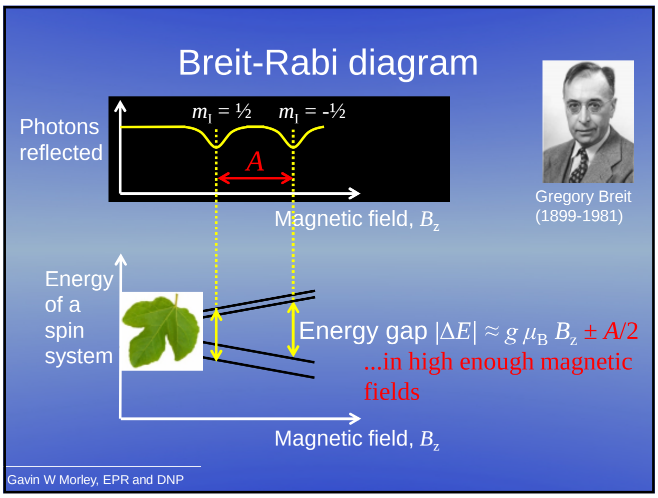


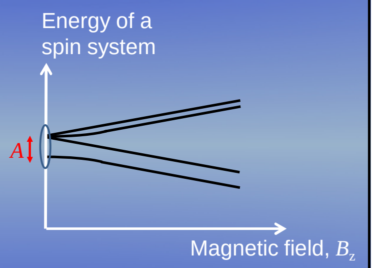
60

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

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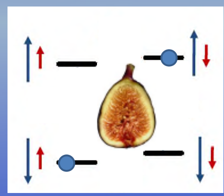
61

Dynamic nuclear polarization (DNP)

Electron paramagnetic resonance (EPR)



more
Forbidden
at high magnetic fields

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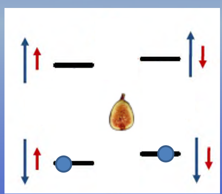
62

Dynamic nuclear polarization (DNP)

Solid effect DNP



also gets weaker at high magnetic fields

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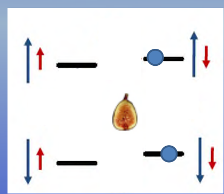
63

Dynamic nuclear polarization (DNP)

Solid effect DNP



also gets weaker at high magnetic fields

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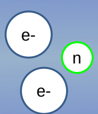
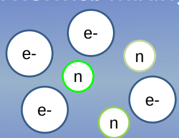
64

Dynamic nuclear polarization (DNP)

Cross effect



Thermal Mixing



also get weaker at high magnetic fields

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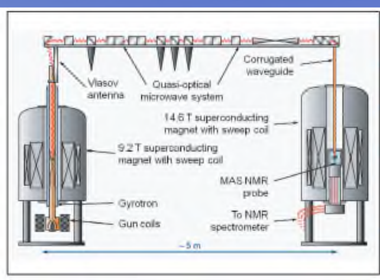
65

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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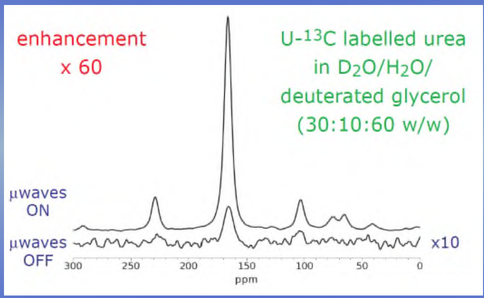
66

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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67

Solid-state DNP

Commercial solid-state DNP-NMR:
400-900 MHz NMR
200x signal enhancement -> 200^2 quicker scans

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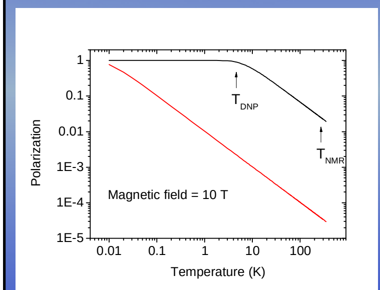
68

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)

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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

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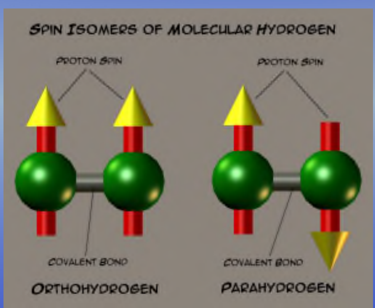
70

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



Hydrogen at low temperatures becomes almost pure parahydrogen

Image by Xaa (Jim Farris)

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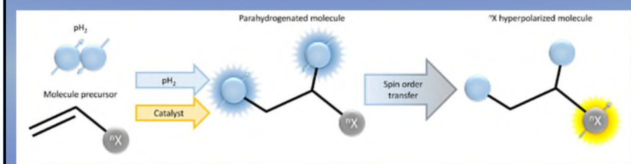
71

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



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.

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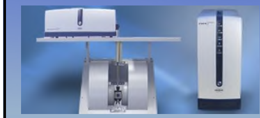
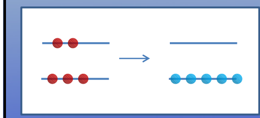
73

Conclusion



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



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

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74