The Radical Pair Mechanism (RPM)

A schematic explanation illustrated by the proposed application to the magnetic compass in animals

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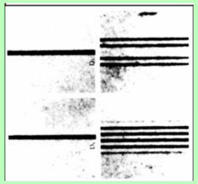
Radical Pair Mechanism (RPM)
– and the chemical compass in the eye*

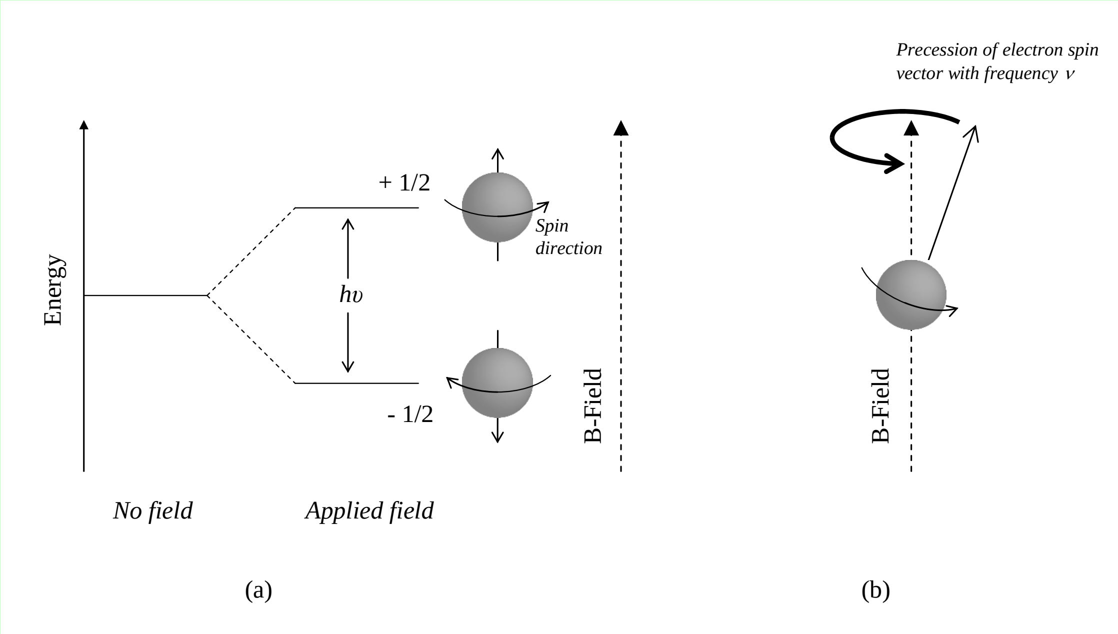
***Note that in salamanders the MF compass is housed in the pineal gland. The gland is also involved in the light-dependent compass in frogs, lizards and some fish**

Introduction to RPM – Zeeman splitting and Larmor precession



Zeeman Effect 1896

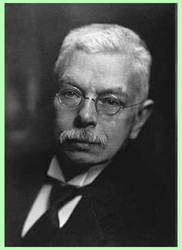
In a static MF, get splitting of spectral lines due to the electron spin



The equivalent classical model has the electron spin vector precessing at the Larmor frequency of 1.4 MHz at 50 μT

Get resonant absorption (ESR) at frequency ν = 1.4 MHz at 50 μT

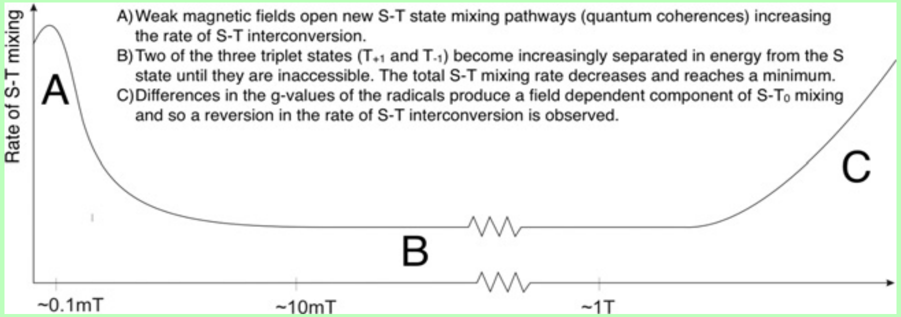
At the GM field in Nottingham, 50 μT:
- hν is ~10^{-7} of thermal energy kT



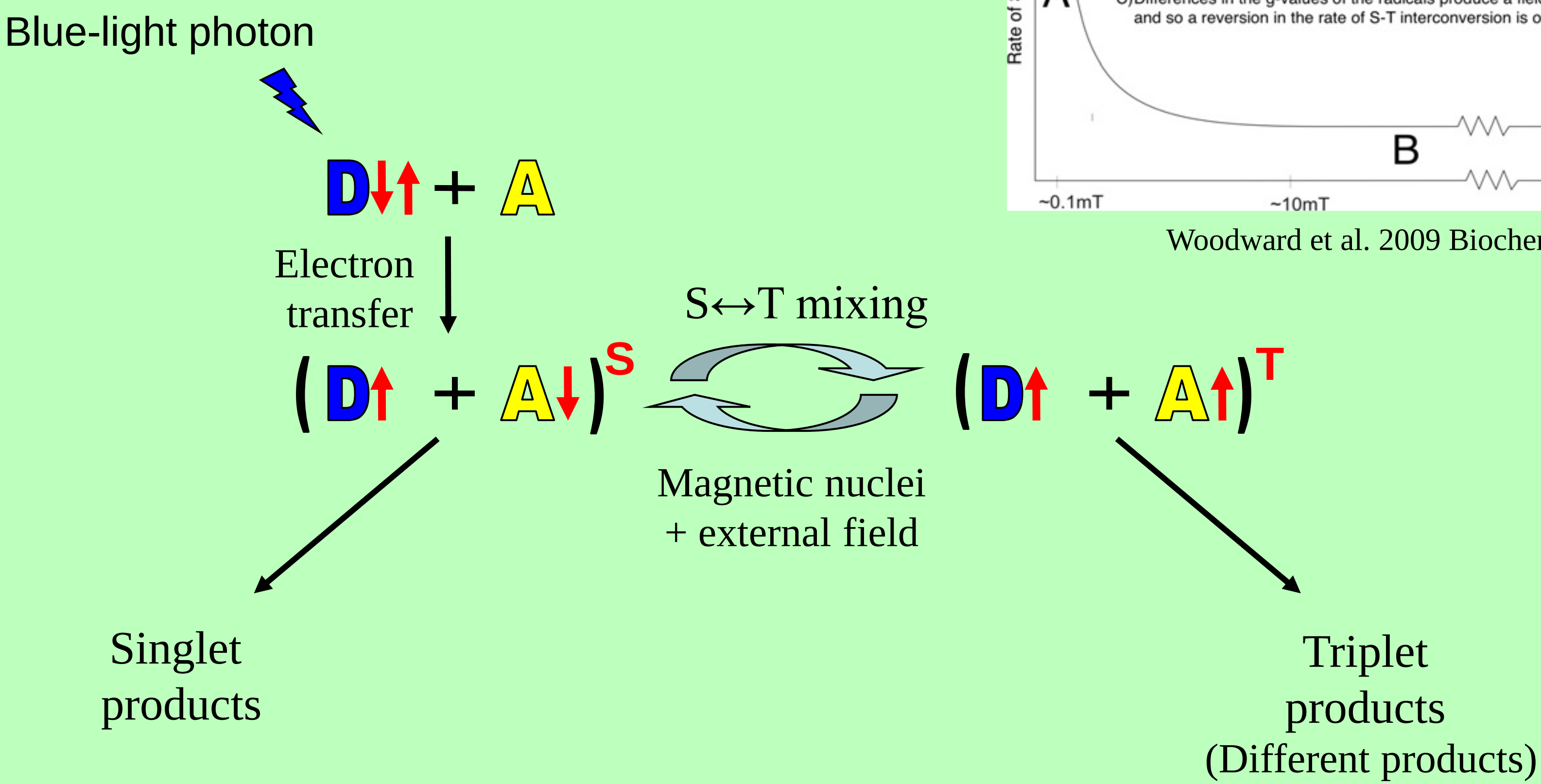
Pieter Zeeman (1865-1943)

Joseph Larmor (1857-1942)

RPM and the Low Field Effect

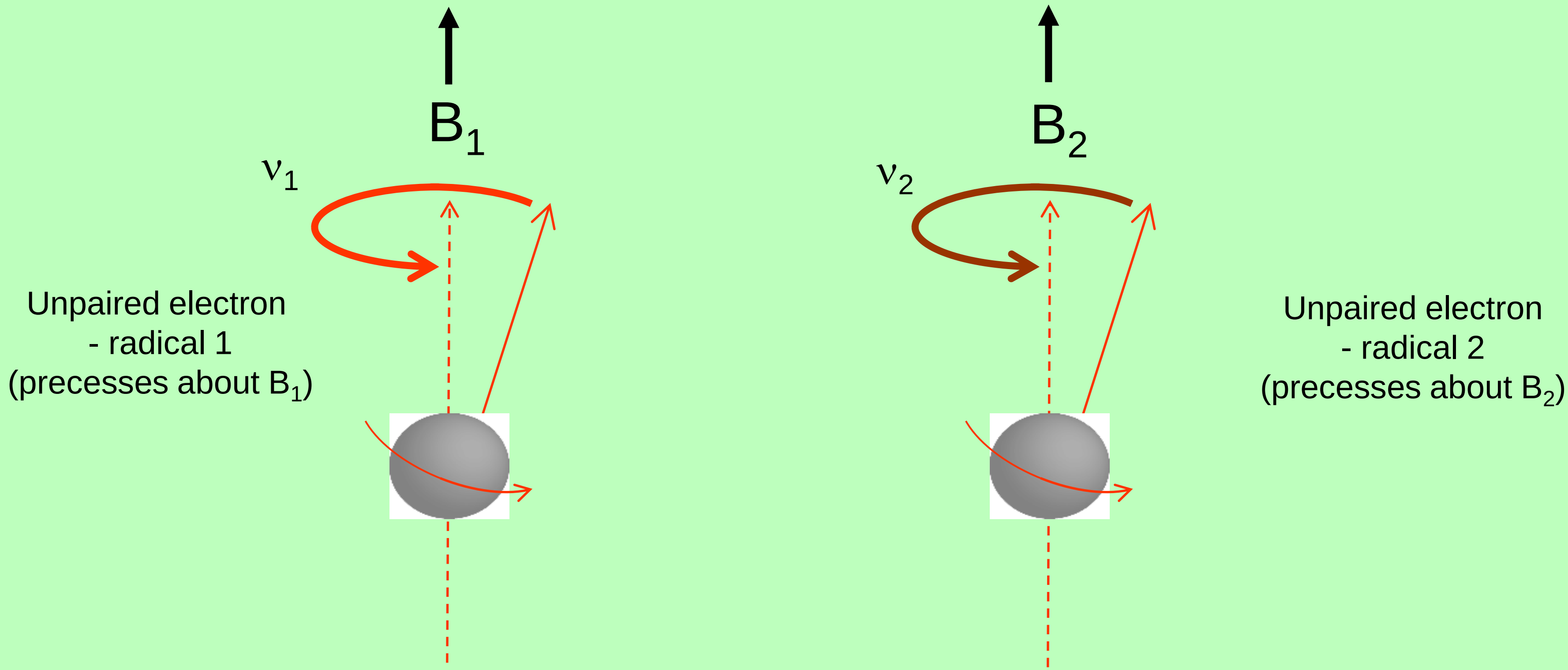


Woodward et al. 2009 Biochem Soc Trans 37(2):358-62.



At low fields* get an increased rate of S-T conversion
T-state radical pairs cannot recombine, so they react elsewhere, e.g. with DNA

*for GM field sensitivity, requires RP lifetimes ~1 us



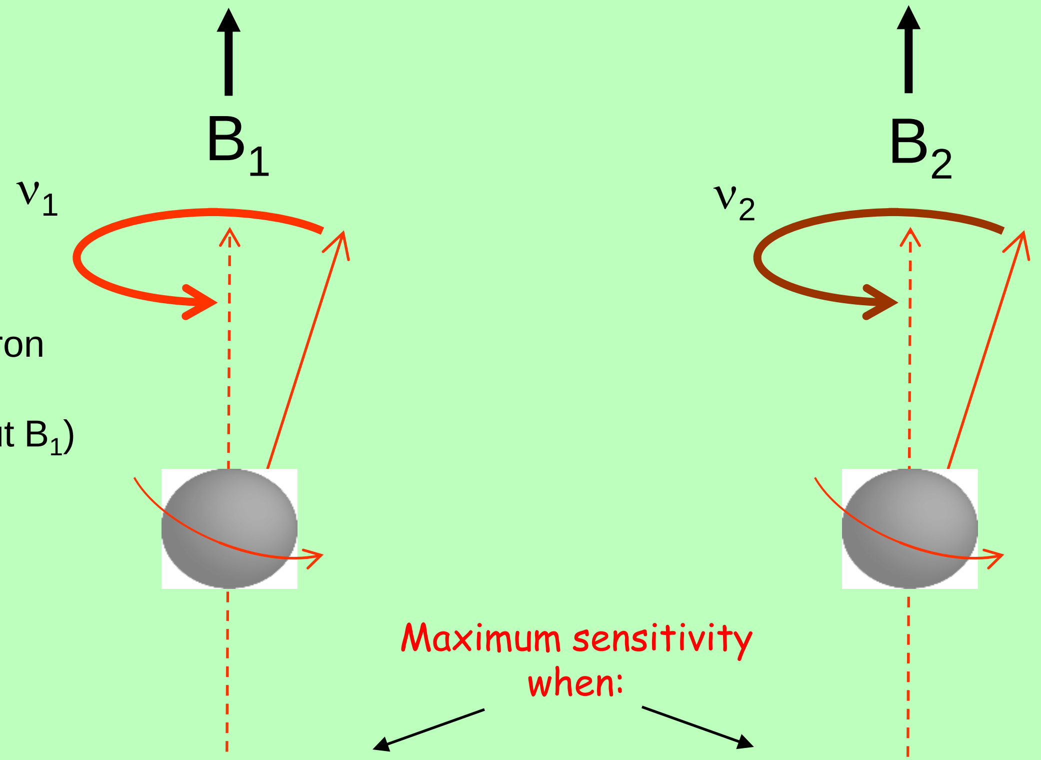
Both radicals see the Earth's magnetic field, 50 μT, in addition to any internal fields

If both radicals experience **the same** MF, no S-T mixing occurs

If each radical experiences **a different** MF, S-T mixing may occur

At the low fields of interest, the radical pair needs to live for ~1 μs, for S-T mixing to evolve

Unpaired electron
- radical 1
(precesses about B_1)



Unpaired electron
- radical 2
(precesses about B_2)

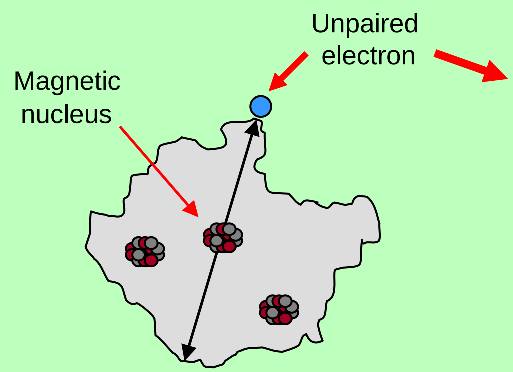
$B_{int} >> B_{ext}$
(Earth's field has little influence)

$B_{int} = 0$,
(only influence is the Earth's field)

The field vector, B comprises:

1) Internal field, B_{int} due to high-abundance magnetic nuclei e.g. ^{1}H ^{14}N

2) External field, B_{ext} – the Earth's field



Hyperfine interactions with the magnetic nucleus ($<10 – 1000$ μT or 28 kHz μT^{-1}):

- s-orbital (isotropic) – part of wave function inside the nucleus
- dipole (anisotropic) – gives compass directionality

Proposal by Ritz et al. 2000

(Biophys J 78:707-718)

-proposed that the MF reception in birds was mediated via the RPM on cryptochromes in the eye

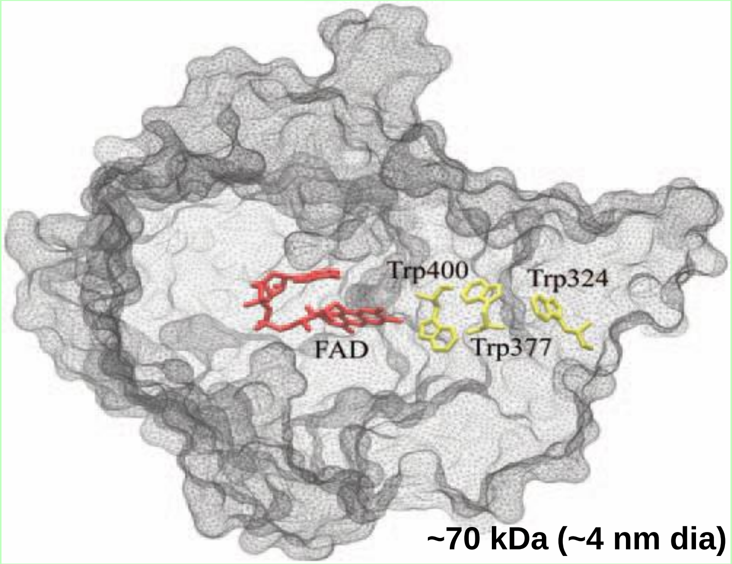
-50–90 kDa blue-light photoreceptor; flavoproteins - **best known for their role in controlling circadian rhythms**. High sequence-homology to DNA photolyases.

Requirements of a chemical compass:

- ✓ produces a radical pair by blue light photon absorption and electron transfer
- ✓ Undergoes increased S-T interconversion in GM field
- ✓ RPs have a lifetime ~1 μs or longer[1]
- ✓ Has an anisotropic response
- ✓ Can be anchored (in the eye)[2]

Ritz proposed that RF fields ~1 MHz might interfere with the MF compass

Schematic view of cryptochrome
(Solov'yov et al. 2007 Biophys J 92:2711–2726)



FAD = flavin-adenine dinucleotide

Radical pair consisting of FADH$^{\bullet}$ and the terminal Tryptophan residue of the cryptochrome Trp-triad,
RP separation is ~1.9 nm (Efimova & Hore 2008)

[1]Liedvogel et al. 2007 *PLos One* 2(10): e1106; [2]Cry1a located in UV/V-cones Niessner et al. 2011 PLoS ONE 6(5): e20091

Radical pair scheme in cryptochrome

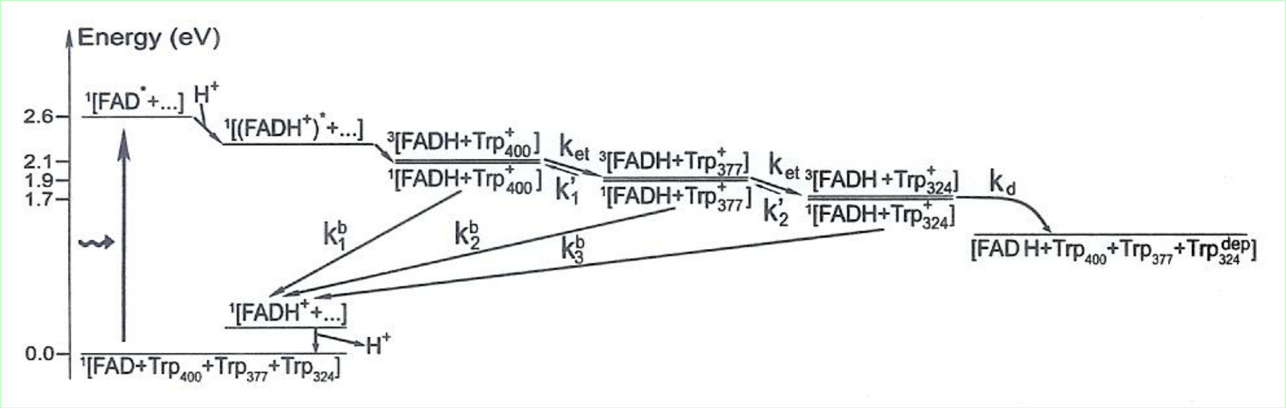


Figure 2. Schematic presentation of the radical-pair reaction pathway in cryptochrome.

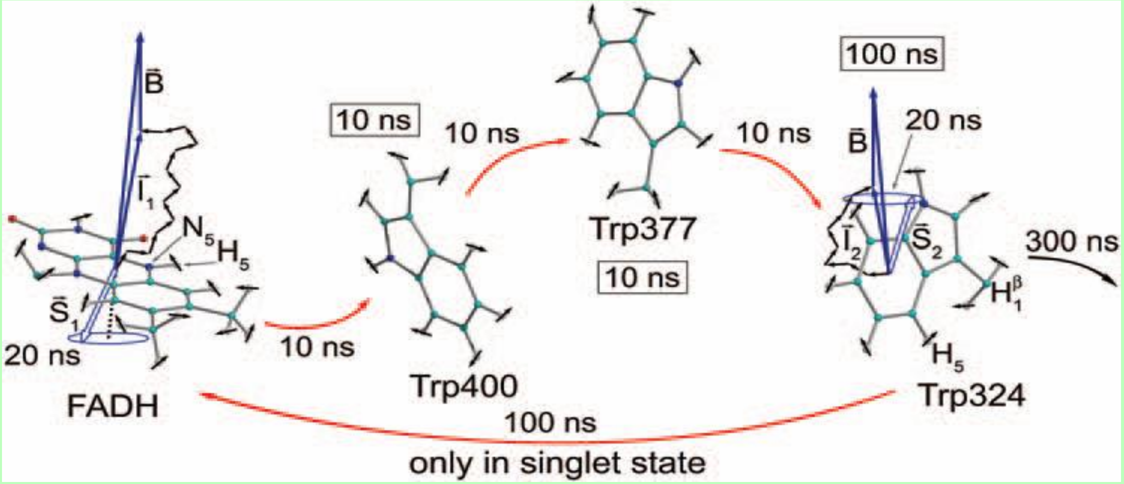


Figure 4 Schematic illustration of electron hole transfer and electron spin dynamics in the FADH cofactor and tryptophan chain.

From Solov'yov et al. (2007) Biophys J 92:2711–2726.

Ritz et al. 2004

Nature 429:177-180

Birds: European robins, *Erithacus rubecula*: 12 individually tested in spring migration season.

MF exposure: Local GMF 46 µT, inclination 66° and 565 nm light (control) plus: (i) broadband 0.1 – 10 MHz, 0.085 µT; (ii) single frequency 7 MHz, 0.47 µT; all parallel, 24° or 48°to GMF vector.

Results:

- RF magnetic fields disrupt the magnetic orientation behaviour of migratory birds.
- Robins were disoriented when exposed to a vertically aligned broadband (0.1–10 MHz) or a single-frequency (7-MHz) field in addition to the geomagnetic field.
- In the 7-MHz oscillating field, effect depended on the angle between the oscillating and the geomagnetic fields.
- Birds exhibited seasonally appropriate migratory orientation with no applied RF or when the RF field was parallel to the geomagnetic field, but were disoriented when it was presented at an angle of 24° or 48° at **0.085 µT**.

Conclusion:

These results are consistent with a resonance effect on singlet–triplet transitions and suggest a magnetic compass based on a radical pair mechanism.

These findings have been replicated in robins and seen in chickens, zebra finches and American cockroaches