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2224-9

School on New Trends in Quantum Dynamics and Quantum Entanglement

14 - 18 February 2011

OUT OF EQUILIBRIUM, DRIVEN OPEN QUANTUM SYSTEMS. TOWARDS QUANTUM EFFECTS IN BIOLOGY.
Part III. The avian compass

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Out of equilibrium, driven open quantum systems

Towards quantum effects in biology

Part III. *The avian compass*

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School on New Trends in Quantum Dynamics and Quantum Entanglement
ICTP, Trieste

Feb. 16, 2011

Institute for Quantum Optics and Quantum Information, Austrian Academy of Sciences
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Plan of the lectures

Part I.

A quantum toolbox for biological systems

- *learning simple mechanisms & ingredients in driven, open quantum systems with spin gases*

Part II.

Conformational-motion induced quantum effects

- *applying the learned concepts to biologically inspired model systems*

Part III.

The avian compass

- *discussing a real world example where quantum dynamics make a difference*

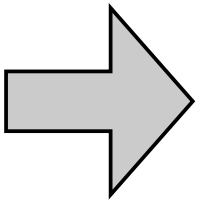
Outline of Part III

- General considerations
- Magneto-reception of birds
- The radical pair mechanism of spin chemistry
- Entanglement in the chemical compass

Can single quantum objects make a difference?

Parts I and II:

Classical backbone structure with
some quantum degrees of freedom



Even if the quantum degrees of freedom
would exhibit quantum effects
in a biological environment,

can the state of few quantum objects
make a difference?

Energy scales

Chemical reactions:

Formation of water:

2.5 eV per molecule

ATP => ADP: 0.3 eV

Green light @500nm:

2.48 eV per photon

Thermal energy @310K: $k_B T$ = 26.7 meV

Electron spin in magnetic field:

$$H = \mu_B g B \frac{\sigma_z}{2}$$

$$\frac{\Delta E}{B} = 1.16 \times 10^{-7} \frac{\text{eV}}{\text{mT}}$$

$\nu/B = 28\,\text{MHz/mT}$ $B_{earth} \approx 0.05\,\text{mT}$

for nuclear spins yet
1000-times smaller
=> completely thermalized

But spins do play a role in chemistry, e.g.

- Pauli-principle => formation of chemical bonds (not considered here),
- **Kinetic effects of internal and external magnetic fields** (spin chemistry)

Avian magneto-reception

- Birds use Earth‘s magnetic field for navigation (migration).
  => Inclination compass

Wiltschko & Wiltschko, Science 1972,
J. Exp. Biol. 1996,
Bioessays 2006

- Effect also established for many other species (e.g. insects)

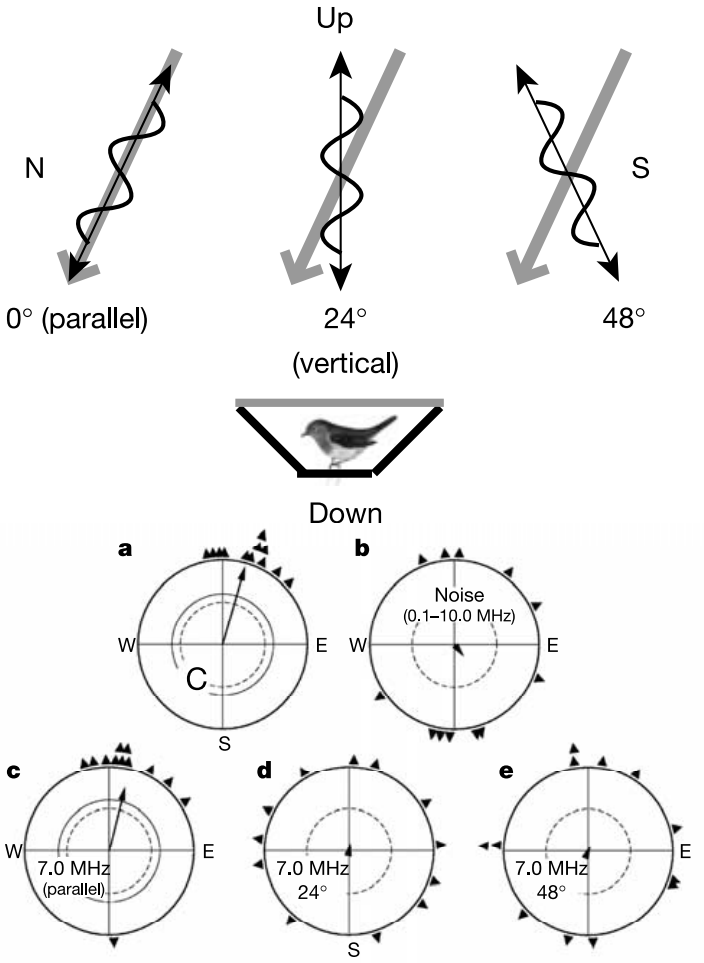
Wiltschko & Wiltschko, Bioessays 2006
Gegear et al. Nature 2008
Burda et al. PNAS 2009
…

- Two main hypotheses for underlying mechanism
  - Magnetite-based mechanism
  - Radical pair chemical reaction mechanism (RPM)

Schulten et al. Z. Phys. Chem. 1978

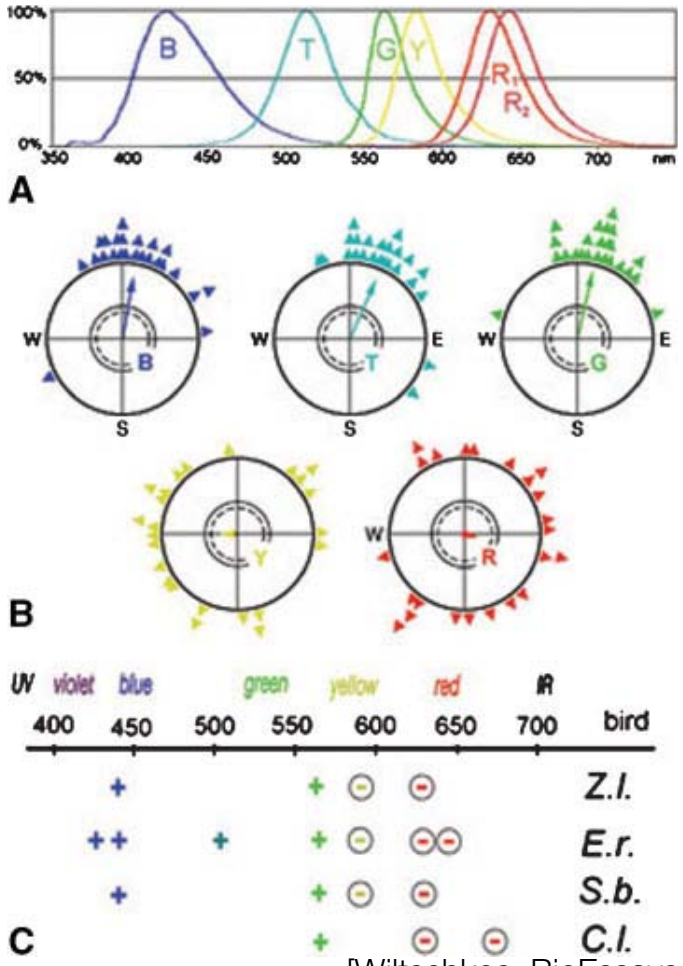
Some experimental data for European Robins

Radio frequency experiments



[Ritz et al., Nature 429, 177, (2004)]

Experiments on light dependence



[Wiltschkos, BioEssays 2006]

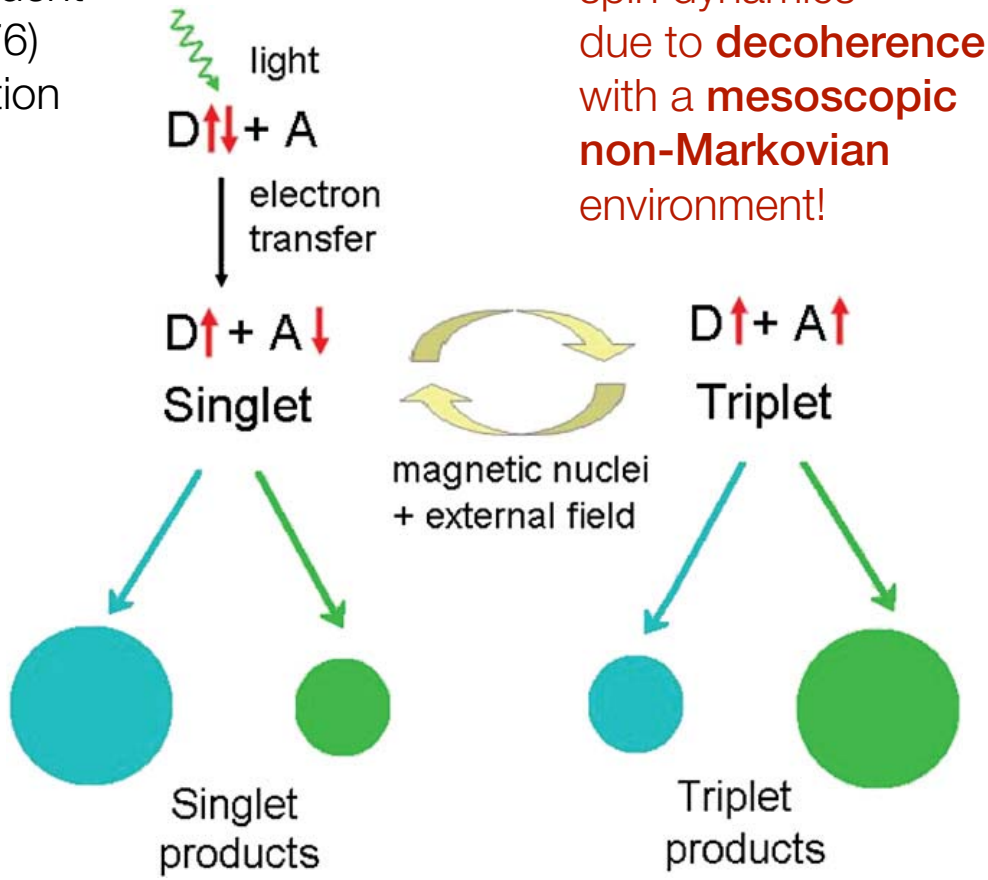
Radical pair mechanism of spin chemistry

Radical Pair Mechanism (RMP):

- Model for spin-/magnetic-field-dependent chemical reaction (Schulten et al. 1976)
- candidate responsible for bird navigation
- well-studied in spin-chemistry (theory + experiment)

Spin chemistry review:
Steiner & Ulrich, Chem. Rev. **89**, 51 (1989).

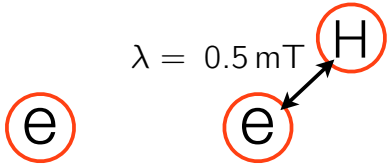
spin dynamics due to **decoherence** with a **mesoscopic non-Markovian** environment!



from Ritz et al. Biophys. J. 96 (2009).

singlet yield = signal
dependent on
- nuclear spins (HF-coupling)
- B-field strength/direction

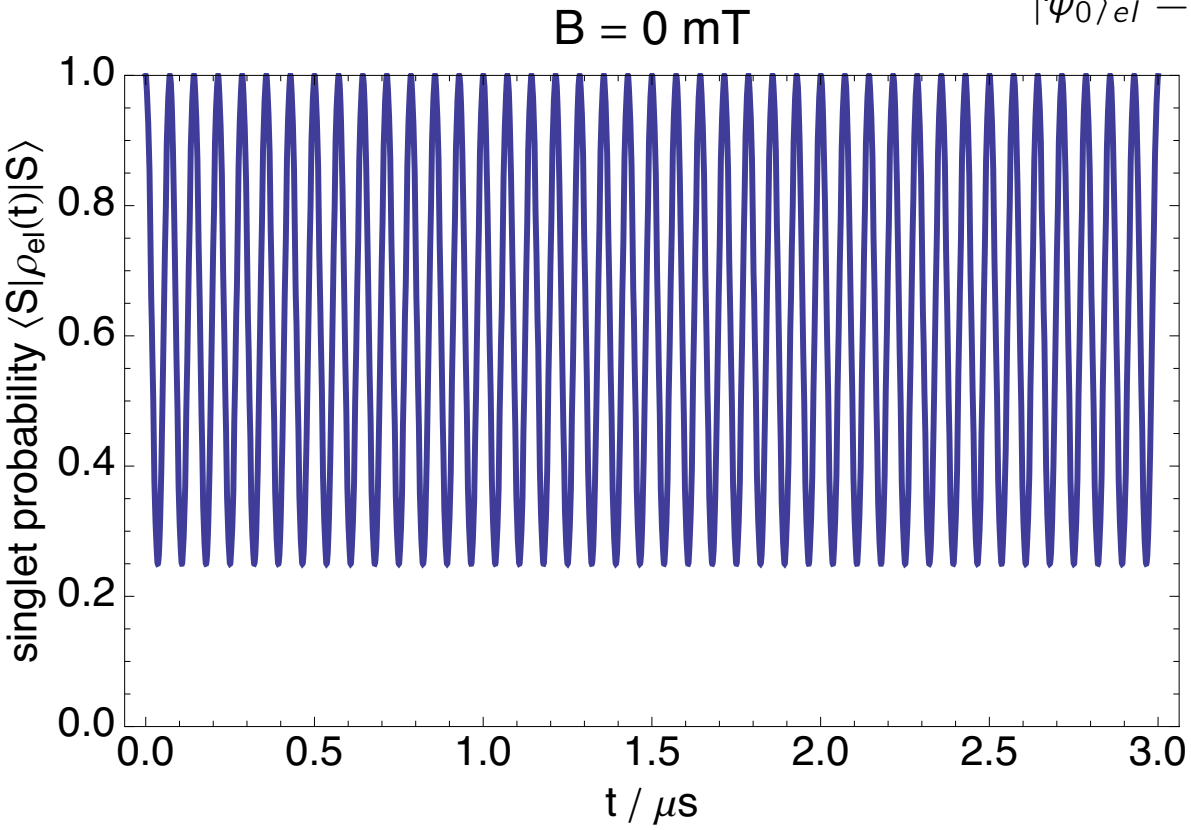
Magnetic field effects in a toy molecule



$$H = -\gamma_e B(S_1^z + S_2^z) + \lambda \vec{S}_1 \cdot \vec{I}$$

$$|\psi_0\rangle_{el} = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} = |S\rangle$$

$$\rho_{nucl}(0) = \mathbb{I}/2$$



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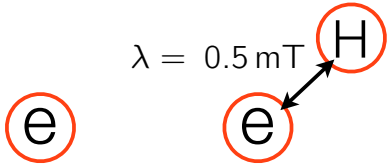

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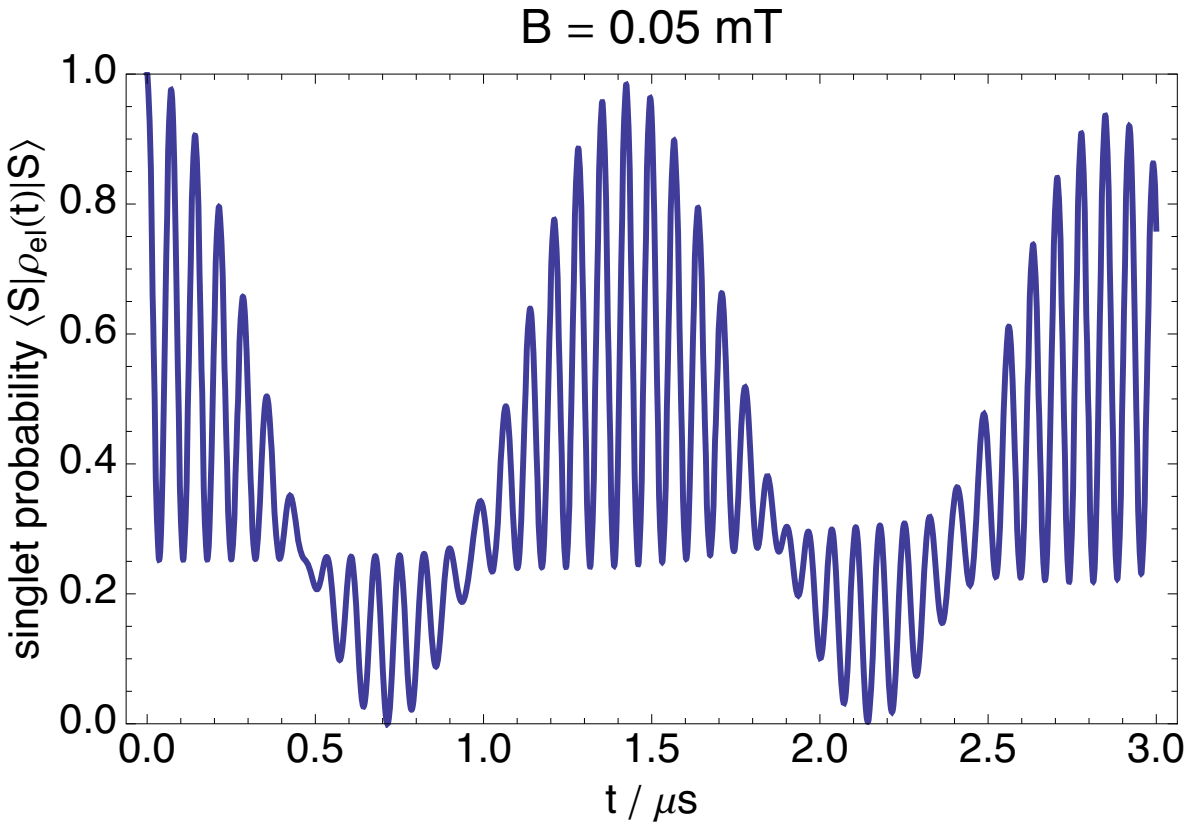
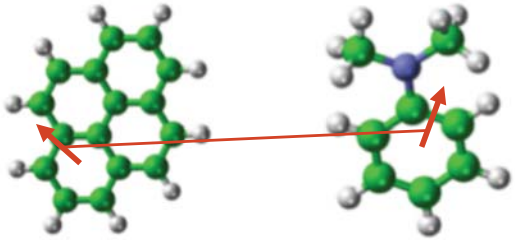


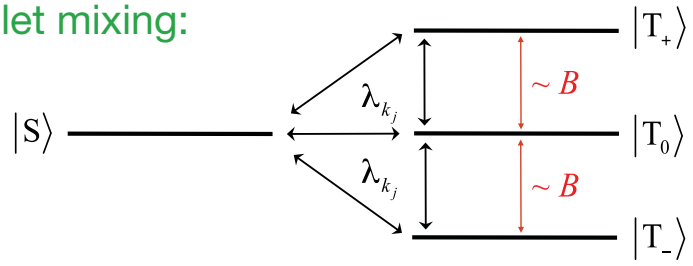
Radical pair mechanism (isotropic hyperfine interactions)

$$H = \sum_{k=1,2} H_c^{(k)} = -\gamma_e B \sum_k S_z^{(k)} + \sum_{k,j} \lambda_{k_j} \vec{S}^{(k)} \cdot \vec{I}^{(k_j)}$$



$[\text{Py-}h_{10}^{\cdot -}\ \text{DMA-}h_{11}^{\cdot +}]$

Singlet-triplet mixing:



Dynamics:

$$\rho_s(t) = \mathrm{Tr}_E \left\{ e^{-iHt} \left[\rho_s(0) \otimes \rho_E(0) \right] e^{+iHt} \right\}$$

$\rho_s(0) = |S\rangle\langle S| \equiv P_S$ singlet state

$\rho_E(0) =$ fully mixed state

$$\longrightarrow \quad \rho_s(t) = \mathcal{M}_t^{(1)} \otimes \mathcal{M}_t^{(2)} \left[P_s \right]$$

completely positive maps (non-Markovian!)

$$|S\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$$

$$|T_0\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right)$$

$$|T_+\rangle = |\uparrow\uparrow\rangle$$

$$|T_-\rangle = |\downarrow\downarrow\rangle$$

Singlet yield

- reaction dynamics quite complicated
  (recombination to singlet/triplet products; quantum description of chemical reactions, e.g. see Kominis vs. Haberkorn vs. Jones & Hore)
- simple phenomenological model:

- **Singlet yield:** $\Phi(t) = \int_0^t r_c(t) f_S(t)\,\mathrm{d}t$

quantum evolution

1) $f_S(t) = \langle \mathrm{S} | \rho_s(t) | \mathrm{S} \rangle$ singlet fraction at re-encounter time

2) $r_c(t) = k e^{-kt}$ exp. distribution of re-encounter times

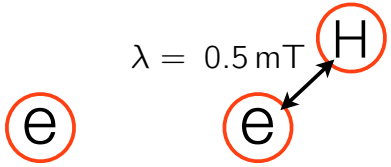
- **Sensitivity:** $\Lambda(B) = \frac{\partial \Phi}{\partial B}$ $\Phi = \Phi(\infty)$

Ad 1) Essential part of dynamics: To study quantities more general than $f_s(t)$,
the full time evolution is computed under nuclear spin environments of $[Py^{\bullet +}\ DMA^{\bullet -}]$

Ad 2) Simple empirical diffusion-type model (classical)

Rodgers et al., J. Am. Chem. Soc. 129 (2007)

Magnetic field effects in a toy molecule



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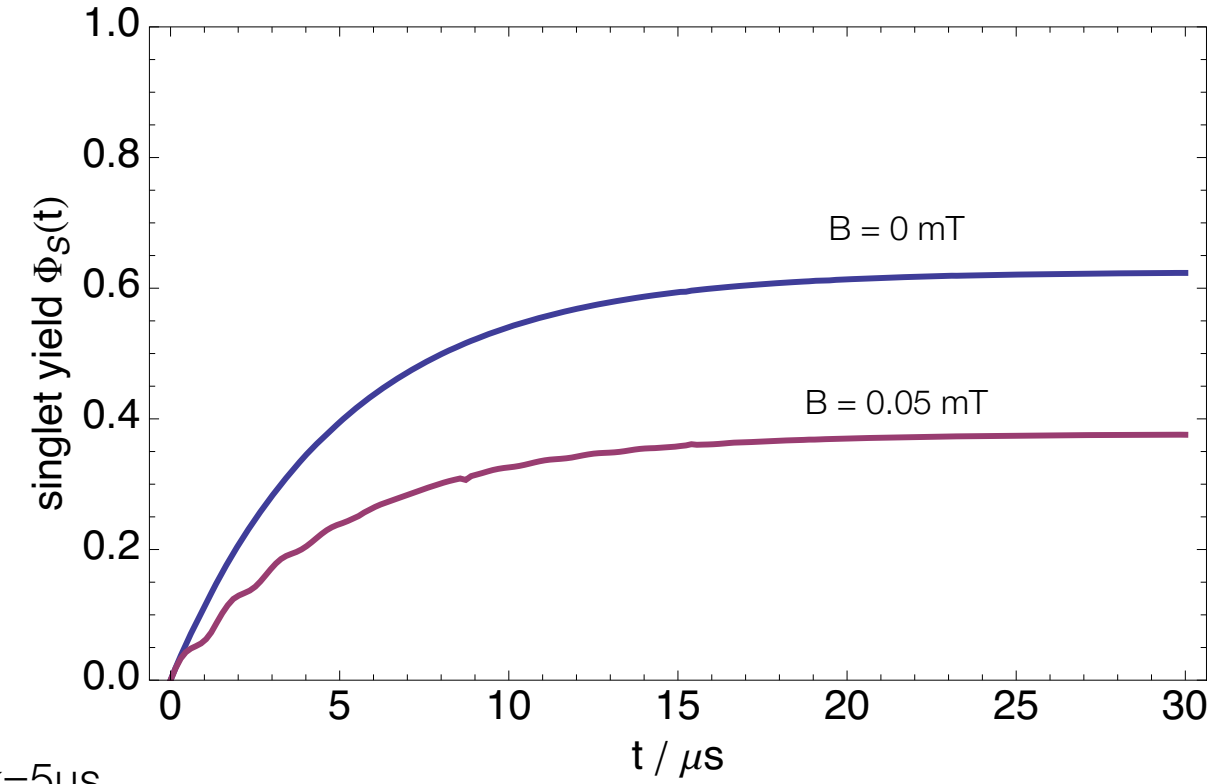
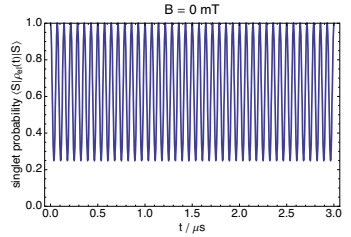
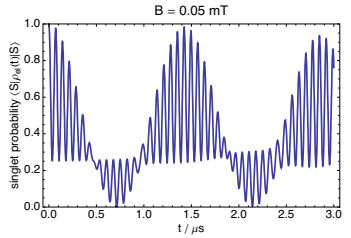


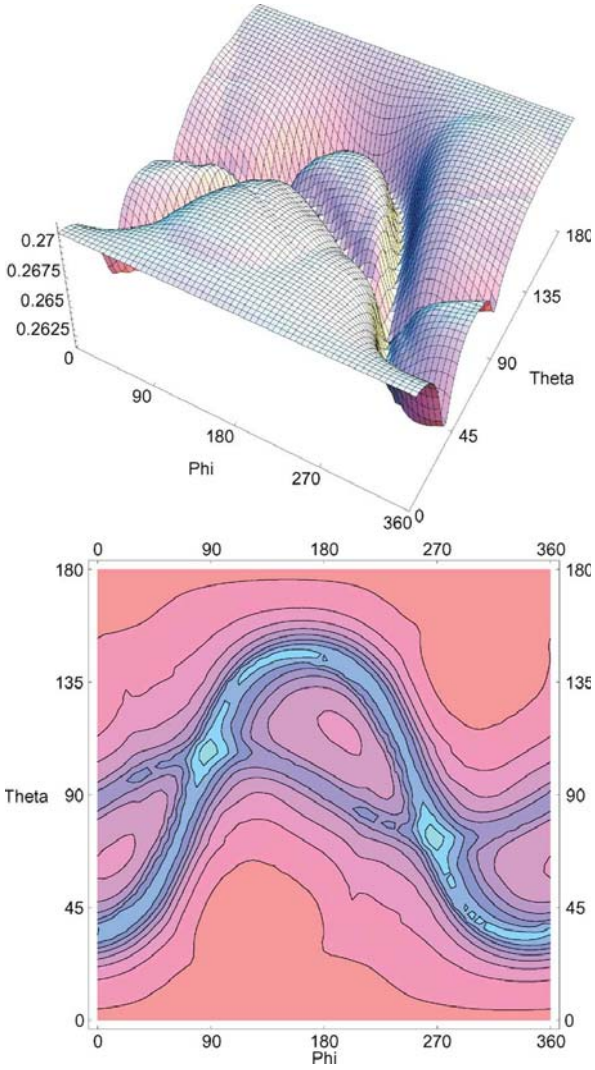




1/k=5μs

=> magnetometer!

Anisotropic field effects

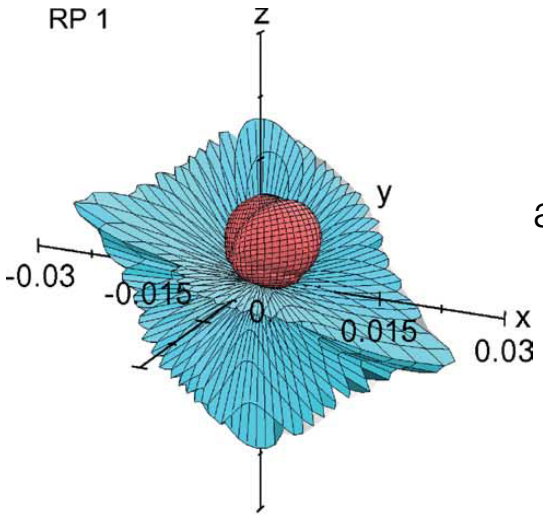


$$H = -\gamma_e \vec{B}(\vec{S}_1 + \vec{S}_2) + \sum_{m=1}^{2} \sum_{k=1}^{N_m} \vec{S}_m \cdot A_{m,k} \cdot \vec{I}_{m,k}$$

anisotropic hyperfine coupling tensor
(fixed to molecule geometry)

$$\vec{B} = B_0(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

$$B_0 = 0.05\,\mathrm{mT}$$

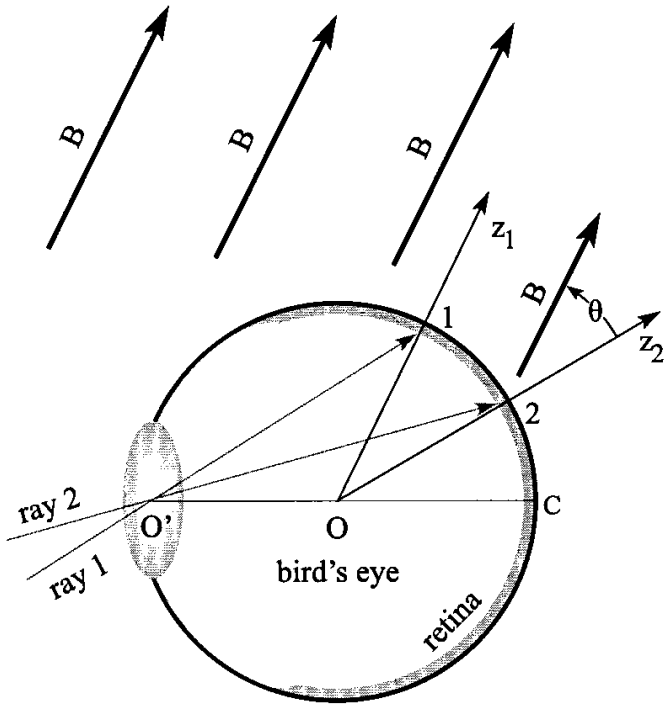


Singlet yield anisotropy for a model molecule of the avian **inclination compass**

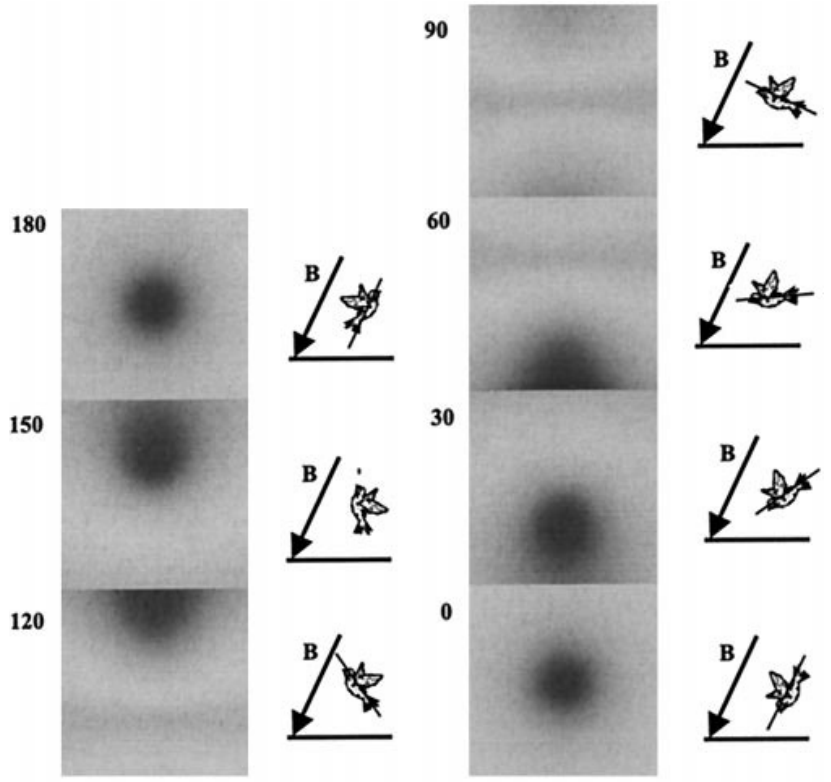
[Cintolesi et al., Chem. Phys. 294 (2003) 385]

Avian magneto-reception via vision

For the anisotropic magnetic field effects to survive, molecules need to be fixed with respect to the magnetic field direction, e.g. oriented in the retina.



Visual modulation patterns if the magnetic field sense piggy-bags the visual pathway.

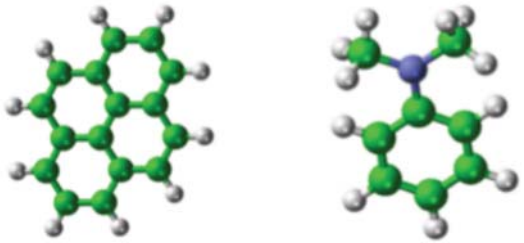


[from Ritz et al., Biophys. J. 78, 707 (2000)]

Specific examples of radical pairs

I

Pyrene Dimethylaniline



$$\mathrm{Py} - h_{10}^{\bullet -} \quad \mathrm{DMA} - h_{11}^{\bullet +}$$

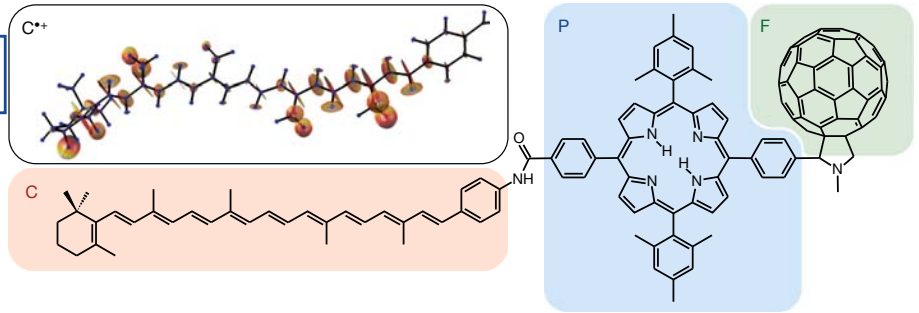
- Well-studied in spin chemistry experiments for mT fields

  Rodgers et al., J. Am. Chem. Soc. **129** (2007)
  Schulten et al. J. Chem. Phys. **67**, 664 (1977)

- **Isotropic** hyperfine coupling => magnetometer
- Radical pair lifetime is short ~10ns

II

Carotenoid-porphyrin-fullerene



C-P-F triad

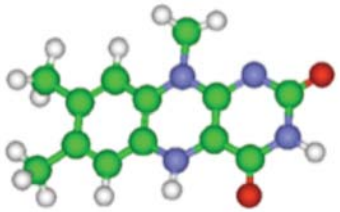
- Magnetic compass model system for **μT fields**

  Maeda et al. Nature **453,** 387 (2008).

- **Non-isotropic** hyperfine coupling => compass
- Radical pair lifetime is rather long ~100 ns

Flavin adenin di-nucleotide
in cryptochrome

III



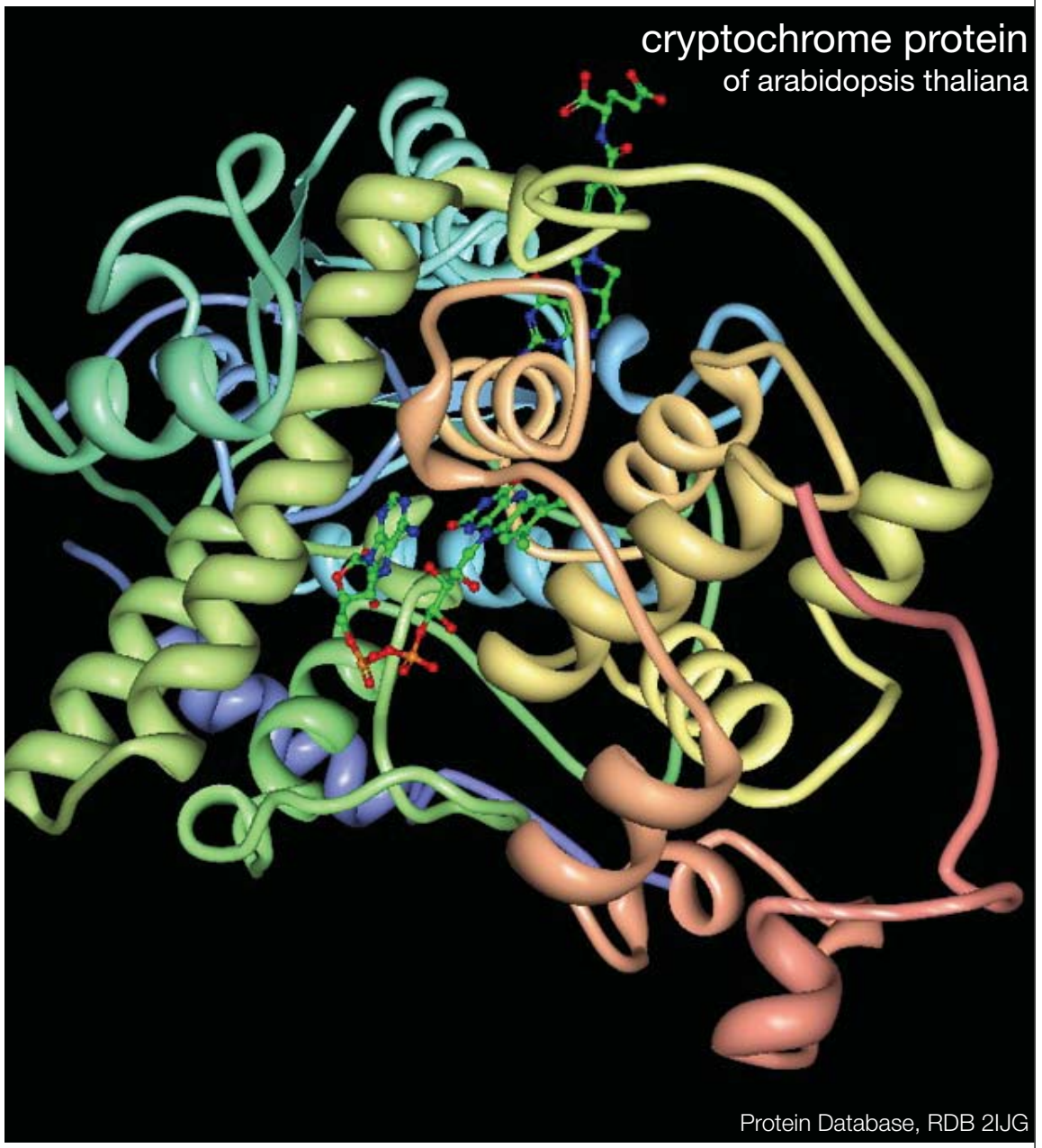
$$FADH^{\bullet} - O_2^{\bullet -}$$

- Current molecular candidate
  for avian compass

  Ritz et al. Biophys. J. **96** (2009).
  Cintolesi et al. Chem. Phys. **294**, 385 (2003)

- Non-isotropic hyperfine coupling

- Radical pair lifetime is long ~**µs**



Questions from a **quantum information** point of view

The dependence of the radical pair mechanism on the entangled singlet state seems to be a quantum effect par excellence!

Which role does **entanglement** play **in the RPM**?

- initial *singlet state* (standard assumption) or just classically correlated?

i.e.

$$\rho_{el}(0) = |S\rangle\langle S|$$

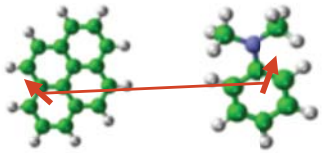
vs. the completely decohered

$$\rho_{el}(0) = (|\uparrow\downarrow\rangle\langle\uparrow\downarrow| + |\downarrow\uparrow\rangle\langle\downarrow\uparrow|)/2$$

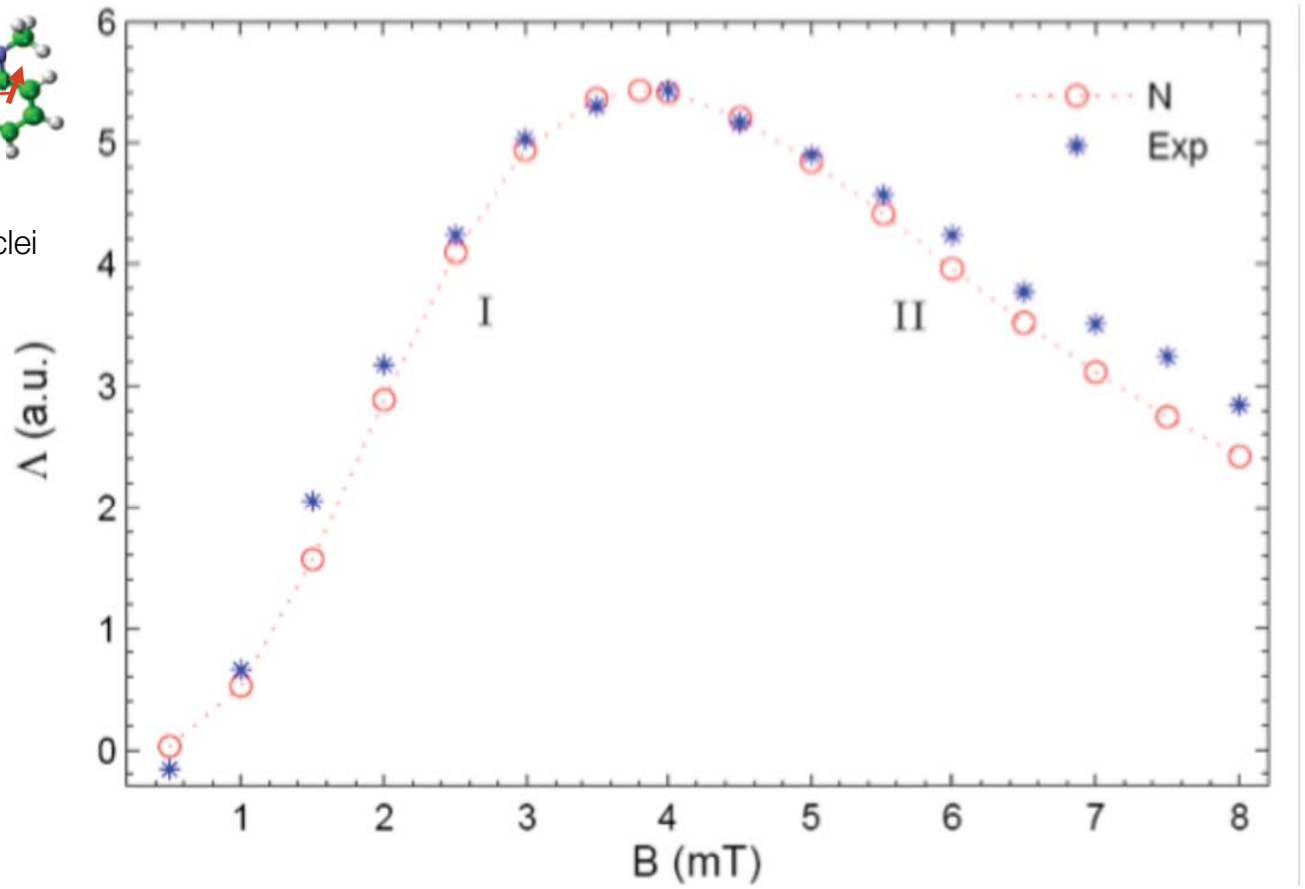
Reference:

J. Cai, G. G. Guerreschi & H. J. Briegel, *Phys. Rev. Lett.* **104,** 220502 (2010)

Magnetic field sensitivity for initial singlet



2 electrons
with 10 + 8 nuclei

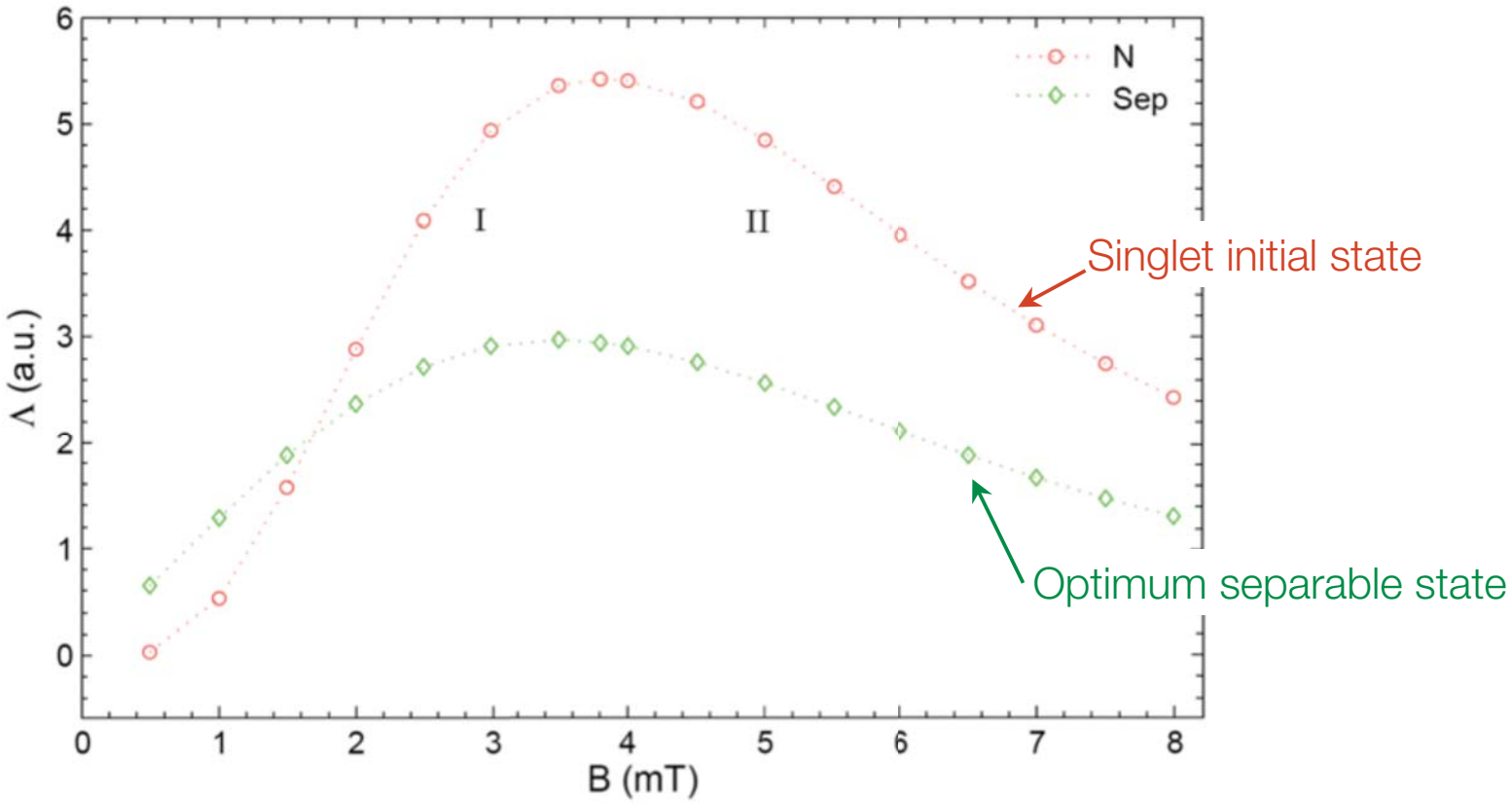


Magnetic field sensitivity of a radical pair reaction $[Py - h_{10}^{\bullet -}\ DMA - h_{11}^{\bullet +}]$ as a function of the magnetic field B. k=5.8 x10^8 s^{-1} [cf. Rodgers et al. (2007)].

Is entanglement relevant?

[Cai et al. *PRL* **104,** 220501 (2010)]

Optimum sensitivity for **separable initial states:**



➢ Entanglement really makes a difference: It is **necessary** for high B-field sensitivity!

Can we distinguish these curves experimentally?

test for presence of initial entanglement by quantum control:
apply π/2-pulse in x-direction, after radical pair creation by photons

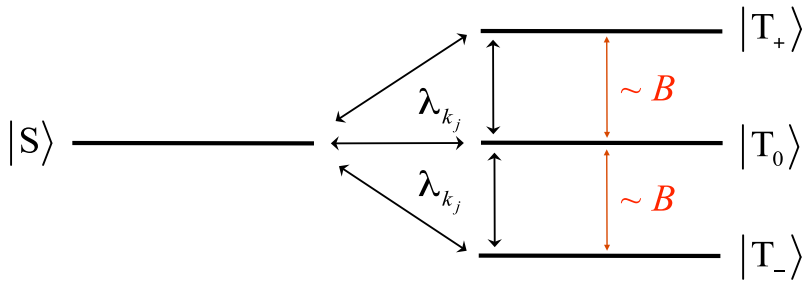
Achievable in principle by using state-of-the-art femto-second laser techniques
& microwave pulses

see. e.g. Maze, Lukin et al. Nature 455 (2008)

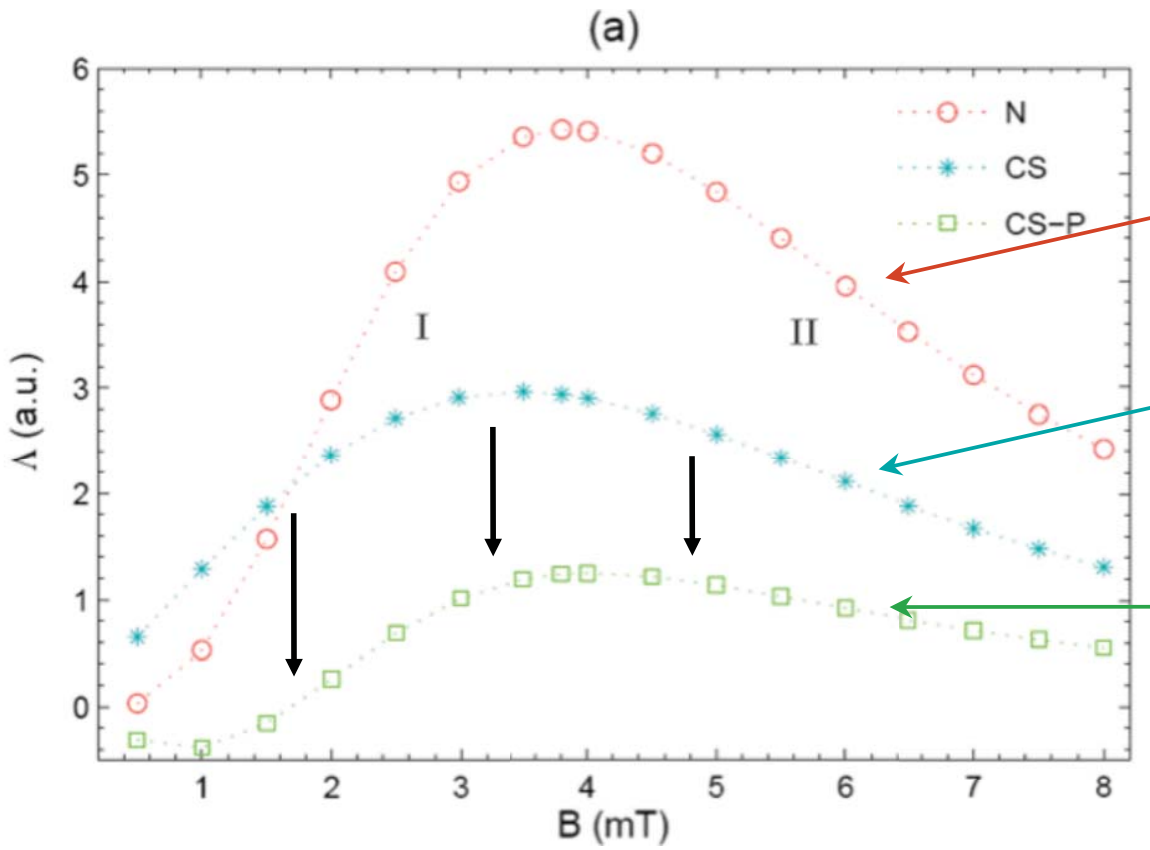
Effect:

$$\left.\begin{array}{rcl} |S\rangle & \longrightarrow & |S\rangle \\ |T_0\rangle & \longrightarrow & |T_+\rangle - |T_-\rangle \end{array}\right\}$$

Singlet remains invariant, while triplet states will mix!



Experimental control pulse effect on sensitivity



singlet

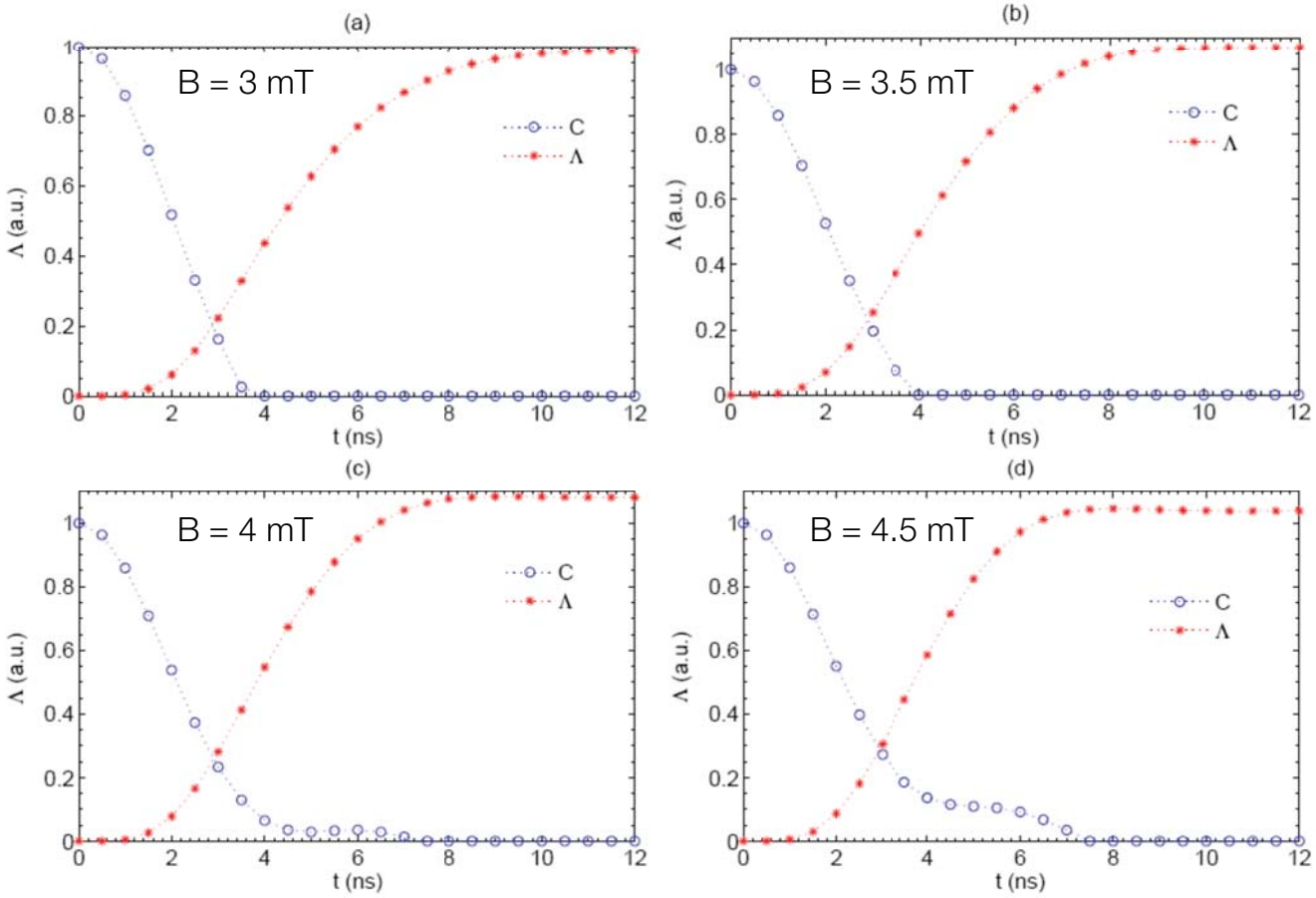
classically correlated

After initial control pulse in along x (singlet is invariant, triplet states mix)

Classical correlations will be revealed by collapse of sensitivity with / without initializing pulse.

Entanglement and field sensitivity

accumulated magnetic-field sensitivity and entanglement evolution in Py-DMA

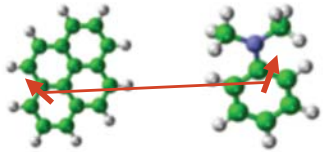


Entanglement lifetime comparable to radical pair lifetime!

Summary:

Entanglement and magnetic-field sensitivity

- standard spin chemistry model system (Py-DMA)
  - entanglement lifetime comparable to radical pair lifetime (ns)
  - sensitivity gap between best separable and best entangled state
  - entanglement necessary for high sensitivity



- avian magneto-reception model (chryptochrome + superoxygen)
  - entanglement lifetime (ns) << radical pair lifetime (μs)
  - best *directional* sensitivity not obtained by the singlet state
    some (randomly found) separable states perform better

    [not shown, see Cai et al., PRL (2010)]
  - bird navigation by means of entanglement is still an open question