Optical control and enhancing sensitivity of chemical magnetometers

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in collaboration with

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Institute for Quantum Optics and Quantum Information, Austrian Academy of Sciences
& Institute for Theoretical Physics, University of Innsbruck

Plan of the talk

- What are chemical magnetometers and what do birds have to do with it?

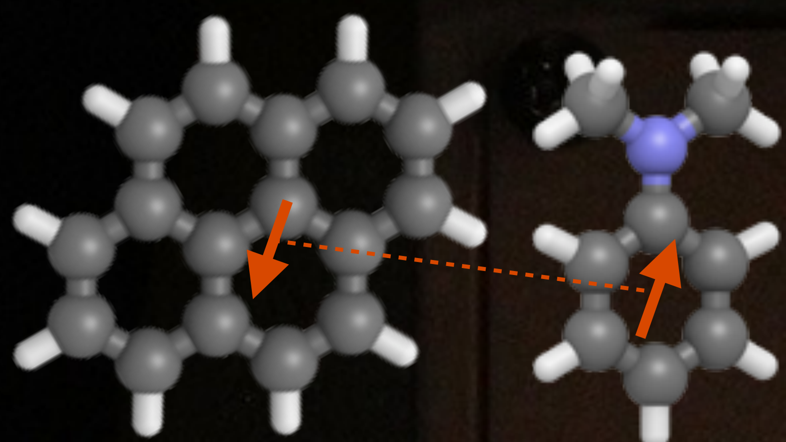
  (=> radical pair mechanism (RPM) and avian magnetoreception)

- Magnetometry with unusual signatures (entanglement lifetime)

- Controlling reaction kinematics with optical switches

  (=> challenges in assessing dynamics of RPM & controlling radical pair systems)

Chemical magnetometer in action



Pyrene N,N-Dimethylaniline

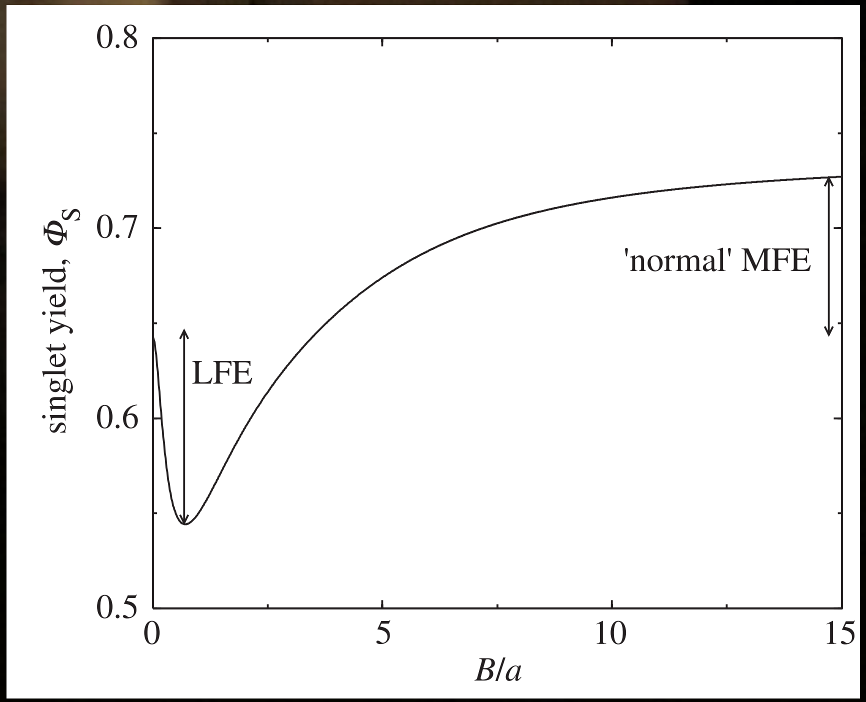
Single electron spin

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

$\nu / B = 28\,\mathrm{MHz/mT}$

$B_{earth} \approx 0.05\,\mathrm{mT}$

Not a shift of chemical equilibrium,
but a spin-dependent kinetic effect.



well studied in spin chemistry,
see e.g. Steiner & Ulrich, Chem. Rev. 89, 51 (1989)

taken from Timmel & Henbest,
Phil. Trans. R. Soc. Lond. A 2004 362

Arndt Lab (Uni Vienna)
Photo by M.T.

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)

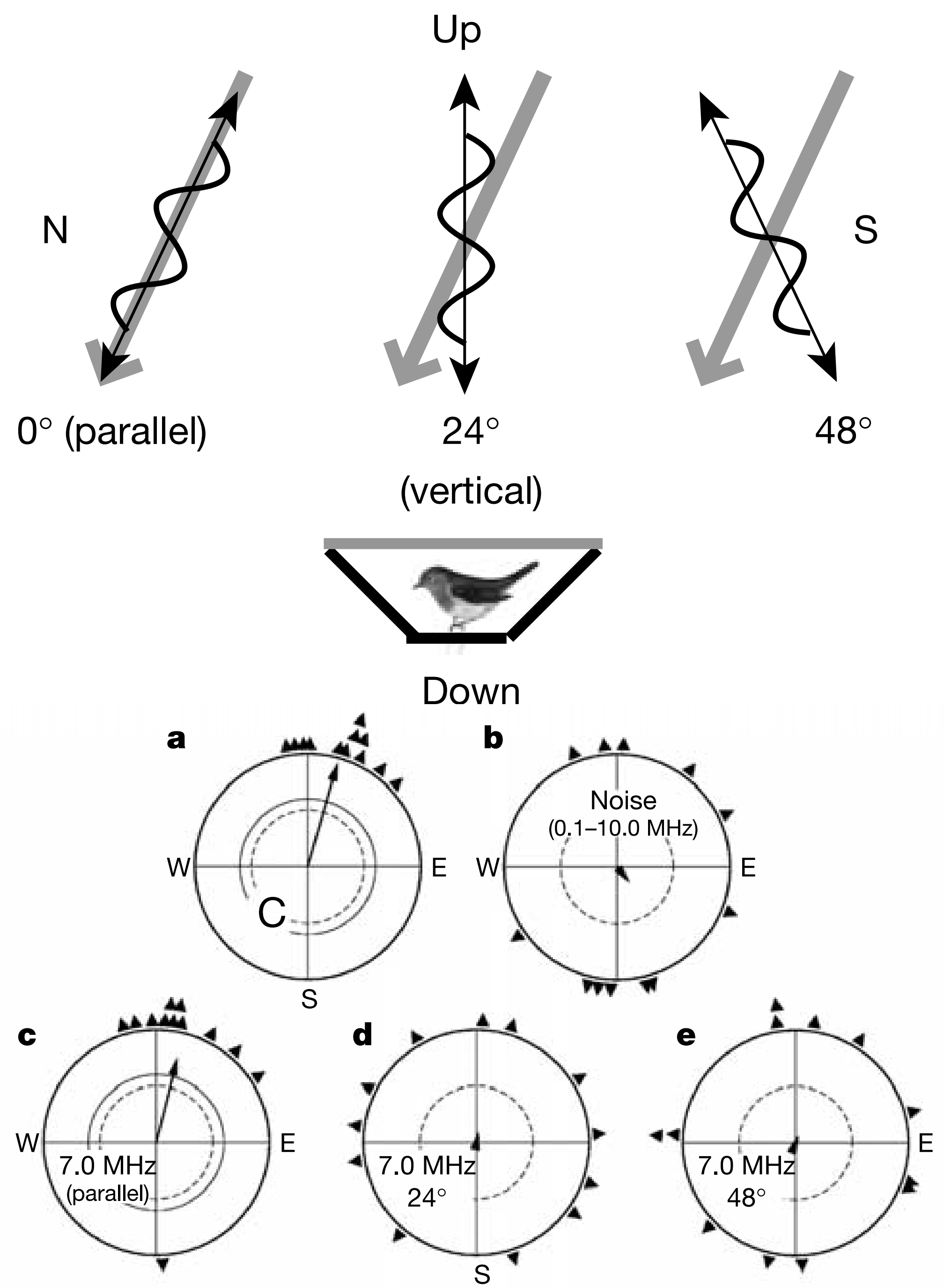
Wiltschko & Wiltschko, Bioessays 2006
Gegear et al. Nature 2008 (=>Drosophila)
Burda et al. PNAS 2009
…

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

Schulten et al. Z. Phys. Chem. 1978

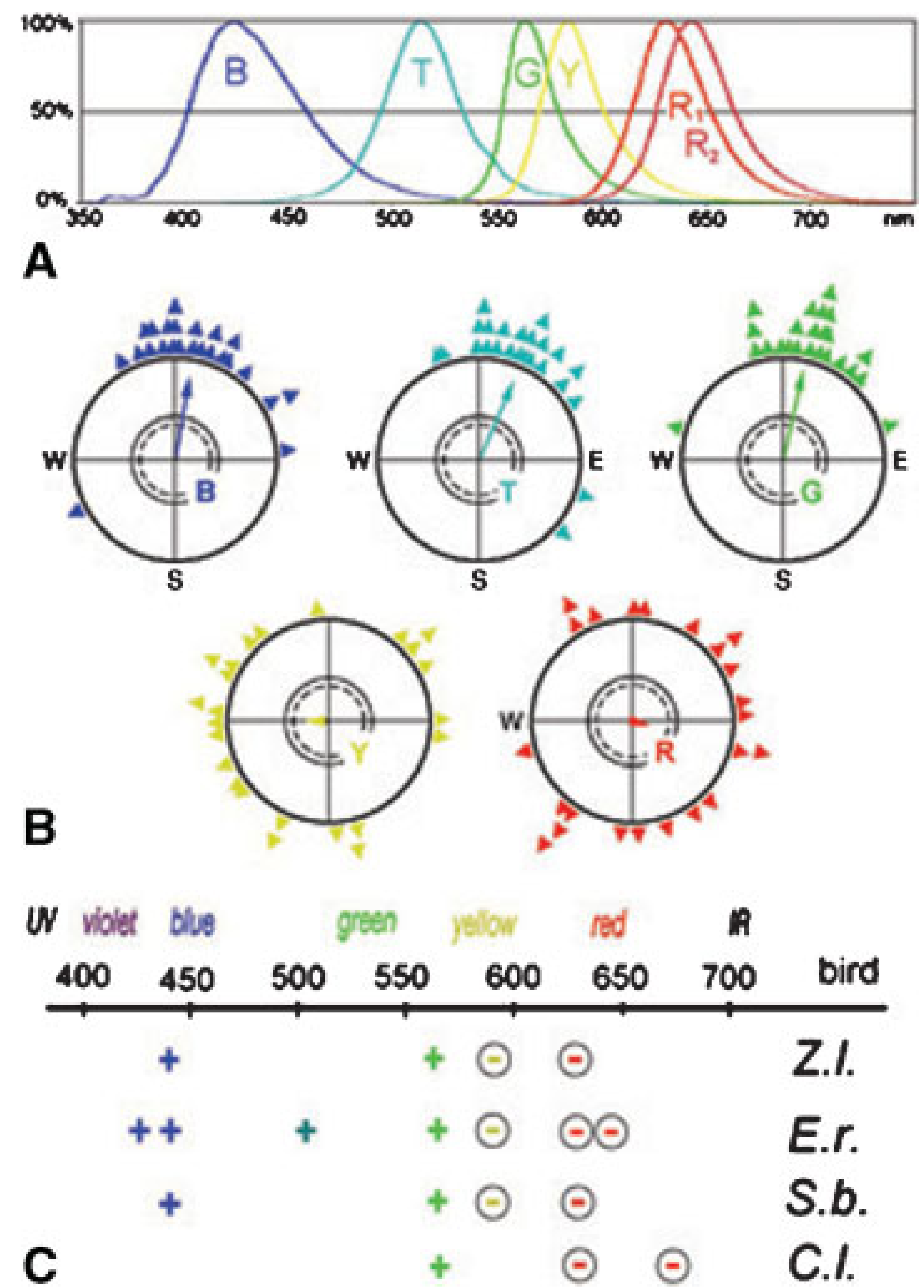
Some experimental data for European Robins

Radio frequency experiments



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

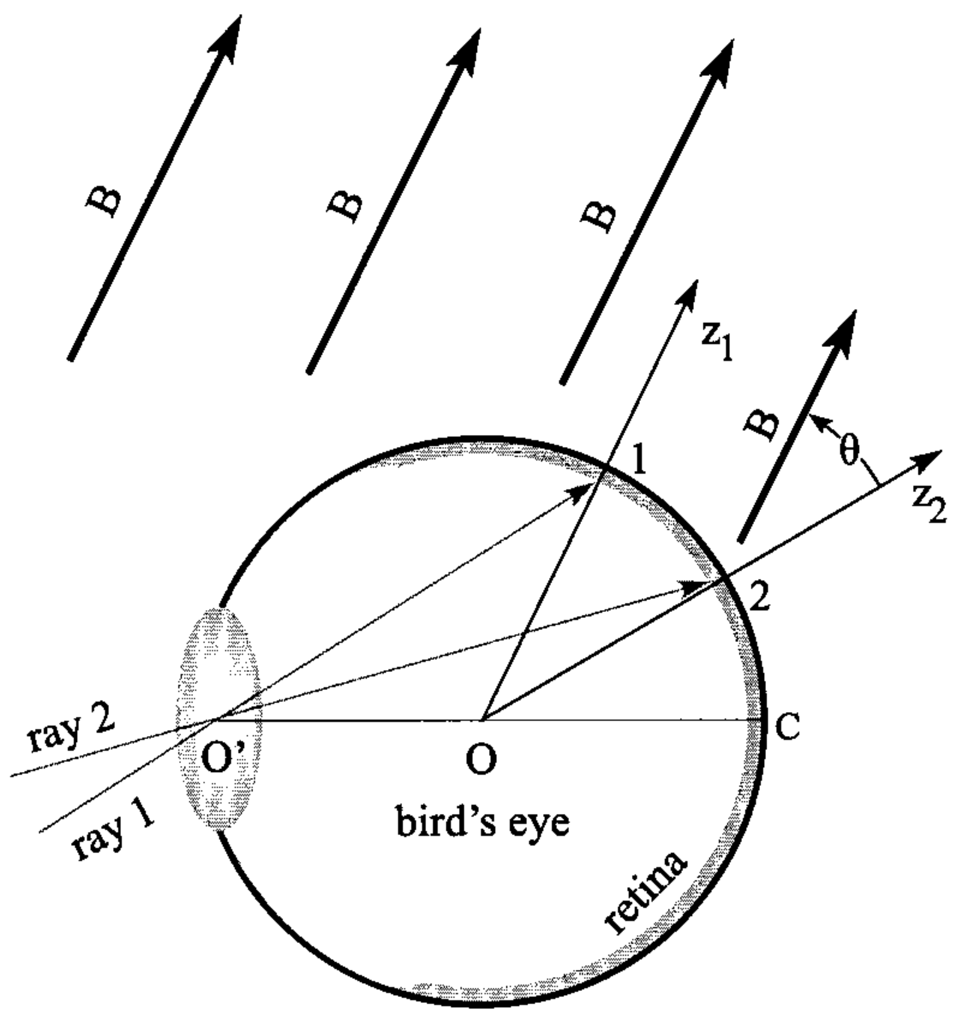
Experiments on light dependence



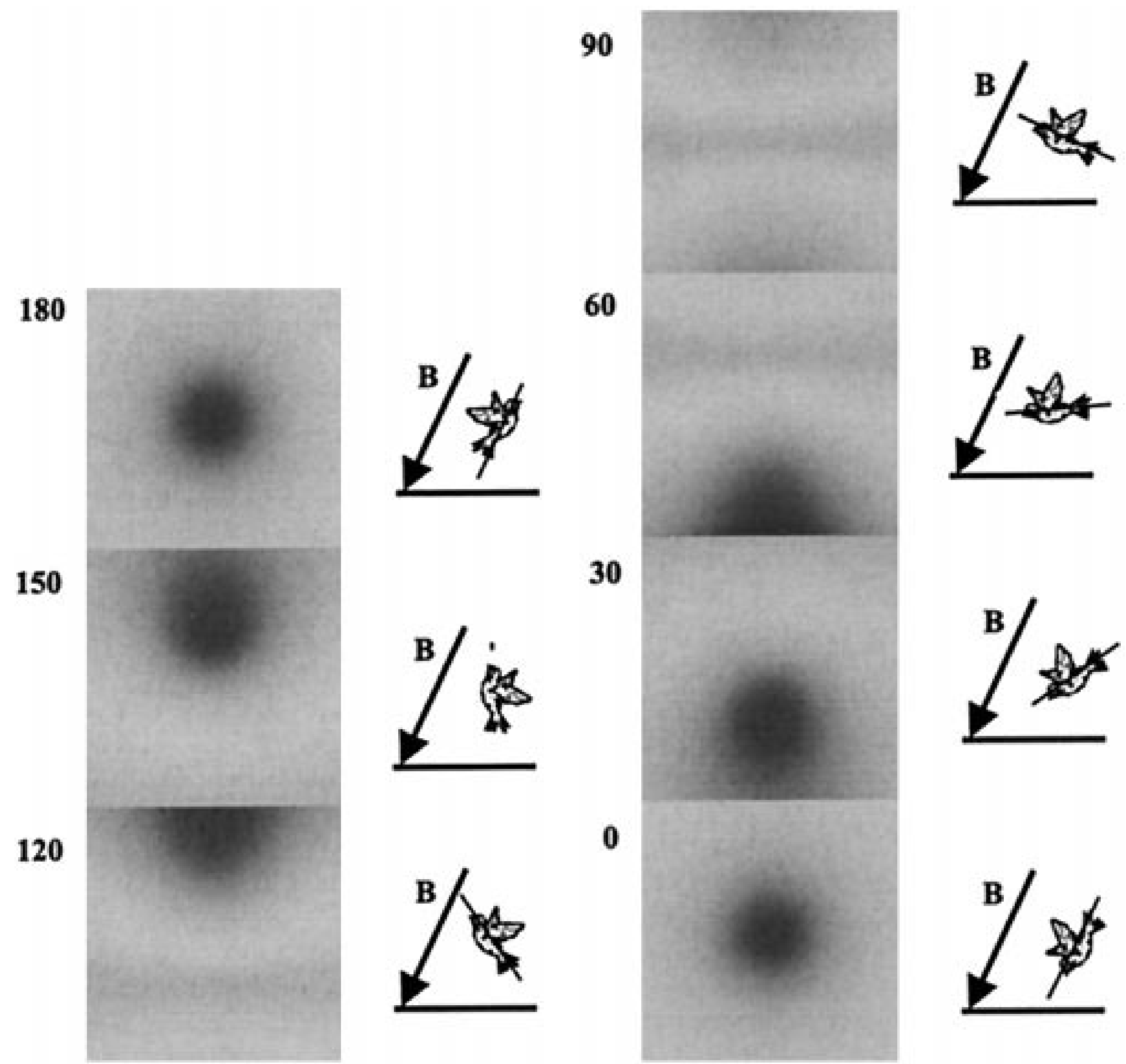
[Wiltschkos, BioEssays 2006]

Avian magneto-reception via vision

For anisotropic magnetic field effects to appear, molecule geometry needs to be fixed with respect to the magnetic field direction, e.g. oriented in the retina.



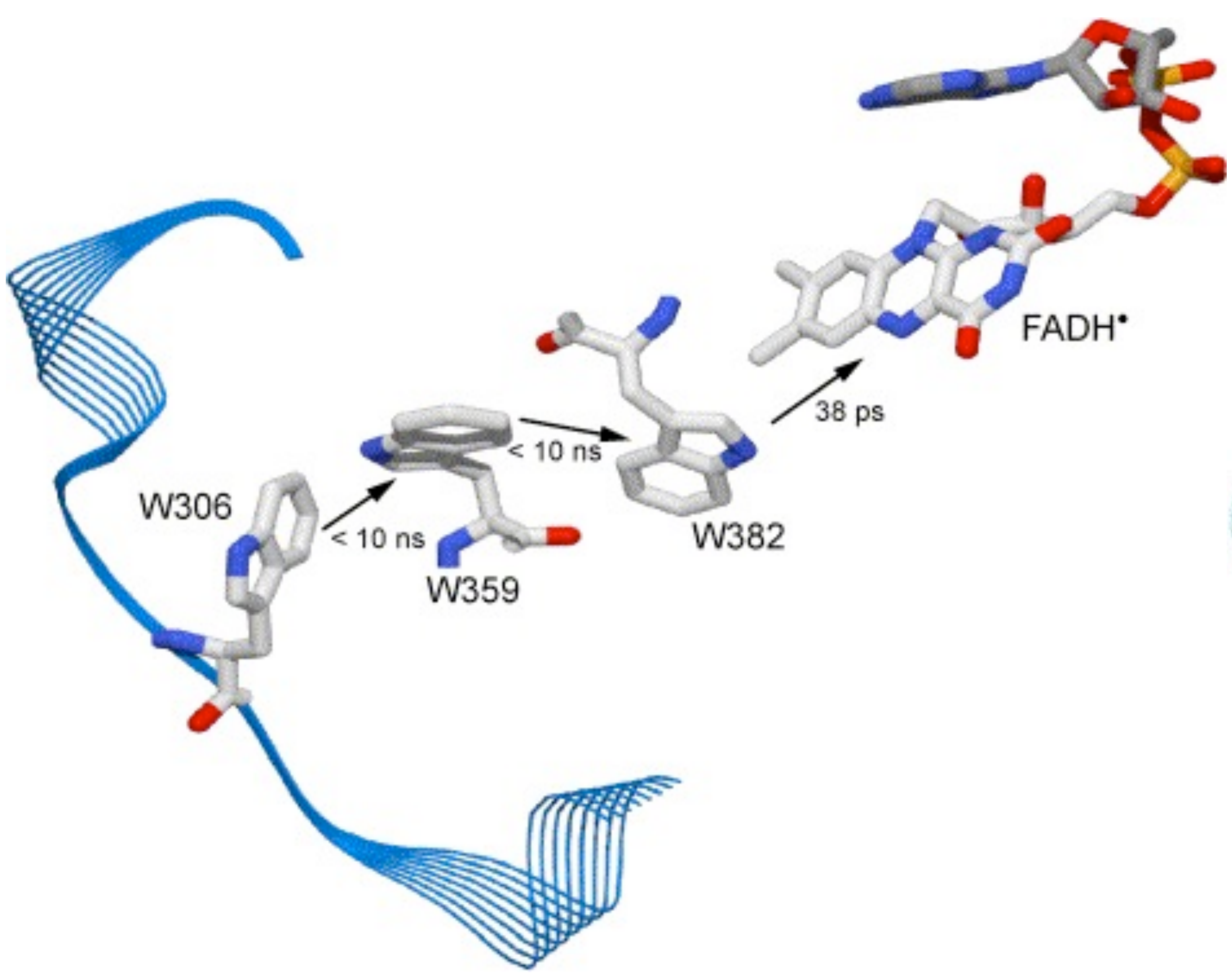
Visual modulation patterns if the magnetic field sense piggy-bags the visual pathway.

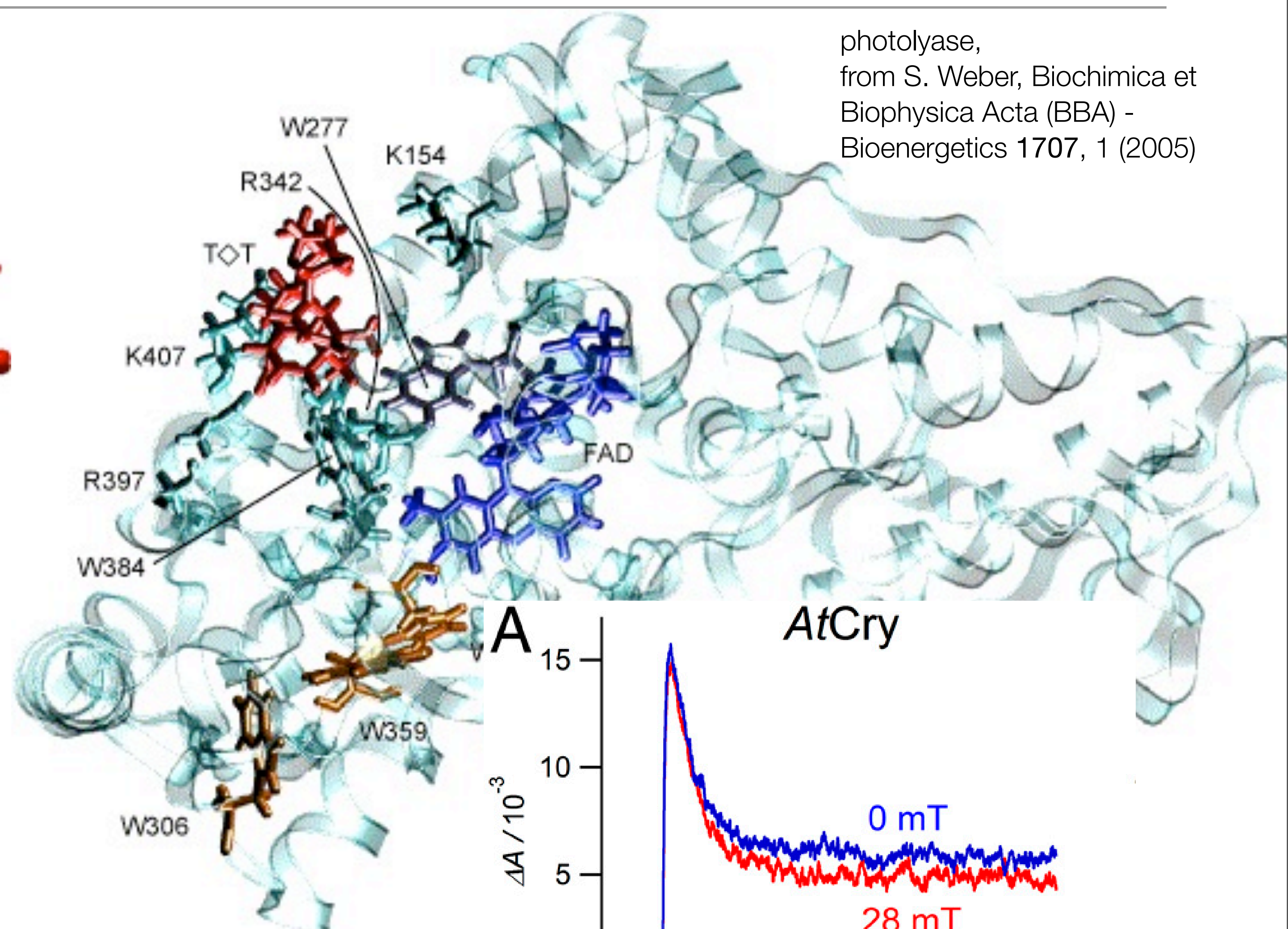


[from Ritz et al., Biophys. J. 78, 707 (2000)]

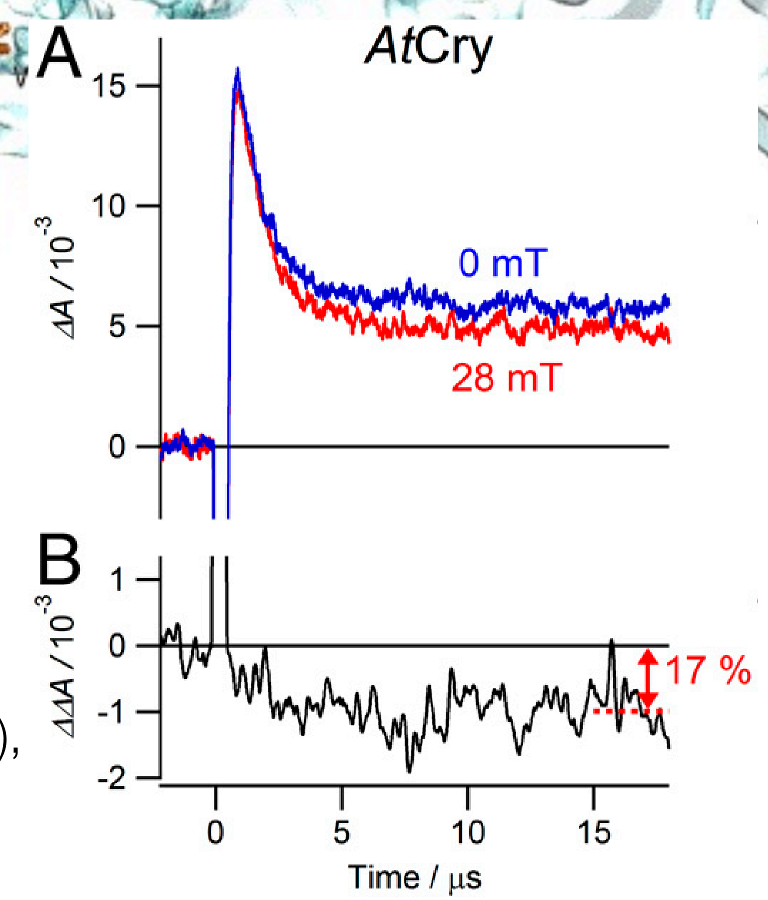
Example of magnetic field effect in proteins

photolyase and cryptochrome
(proteins with a flavin cofactor)





photolyase,
from S. Weber, Biochimica et Biophysica Acta (BBA) - Bioenergetics **1707**, 1 (2005)

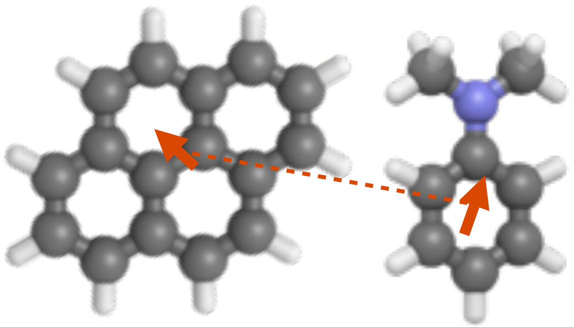


radical pair:
flavin (FAD/FADH)
tryptophan residue

Magentic field effects for photolyase and cryptochrome (Fig.) observed in vitro:

Henbest et al. PNAS **105**, 14395 (2008),
Maeda et al. PNAS 109, 4774 (2012).

The radical pair mechanism



Spin Hamiltonian:

$$H = \sum_{m=1,2} \left[-\gamma_e \left(\vec{B}_{ext} + \vec{B}_c(t) \right) \cdot \vec{S}_z^{(m)} + \sum_n \lambda_{m_n} \vec{S}_m \cdot \vec{I}_{m_n} \right]$$

energy

$A + {}^S D^*$

excited state

electron transfer

photo-excitation

$^S[A^{\bullet -} + D^{\bullet +}]$ $\quad$ $^T[A^{\bullet -} + D^{\bullet +}]$

$|S\rangle$ $\quad$ $|T_+\rangle$, $|T_0\rangle$, $|T_-\rangle$ $\quad$ $\sim B$ $\quad$ $\sim B$

radical pair

spin-selective reaction

singlet product

e.g. recombined ground state, fluorescence

triplet product

e.g. recombined triplet-excited state

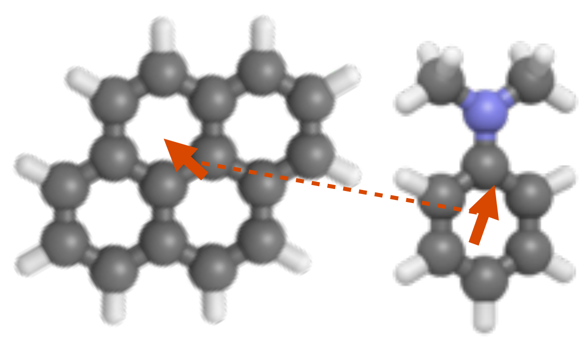
$A + D$

molecular ground state

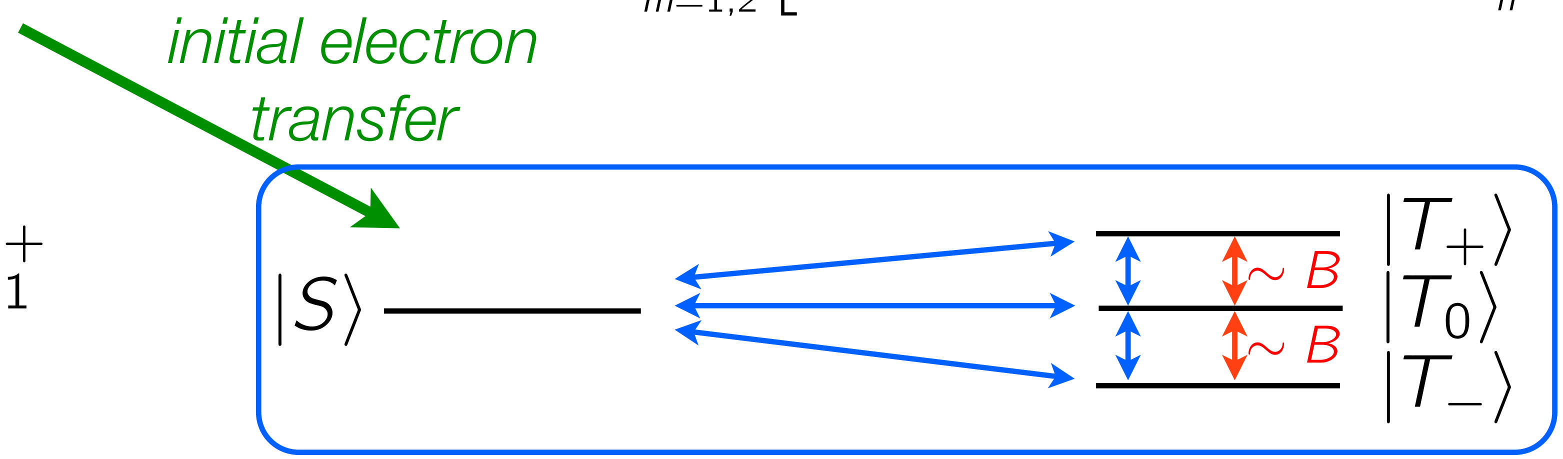
Nuclear spin bath

Spin Hamiltonian:

$$H = \sum_{m=1,2} \left[-\gamma_e \left(\vec{B}_{ext} + \vec{B}_c(t) \right) \cdot \vec{S}_z^{(m)} + \sum_n \lambda_{m_n} \vec{S}_m \cdot \vec{I}_{m_n} \right]$$



$\text{Py–}h_{10}^{\bullet -}$ $\text{DMA–}h_{11}^{\bullet +}$



Decoherence due to local nuclear spin baths breaks symmetry and enables the magnetometer.

System dynamics

system: electron spins
environment: nuclear spins (mesoscopic)

$$\rho_{\text{sys}}(t) = \text{Tr}_{\text{env}} \left\{ e^{-iHt} \left[\rho_{\text{sys}}(0) \otimes \rho_{\text{env}}(0) \right] e^{+iHt} \right\}$$

$$\rho_{\text{sys}}(0) = |S\rangle\langle S| \qquad \rho_{\text{env}}(0) \propto \mathbb{I}$$

completely positive maps (non-Markovian) ⟶ $\rho_{\text{sys}}(t) = \mathcal{M}_t^{(1)} \otimes \mathcal{M}_t^{(2)} |S\rangle\langle S|$

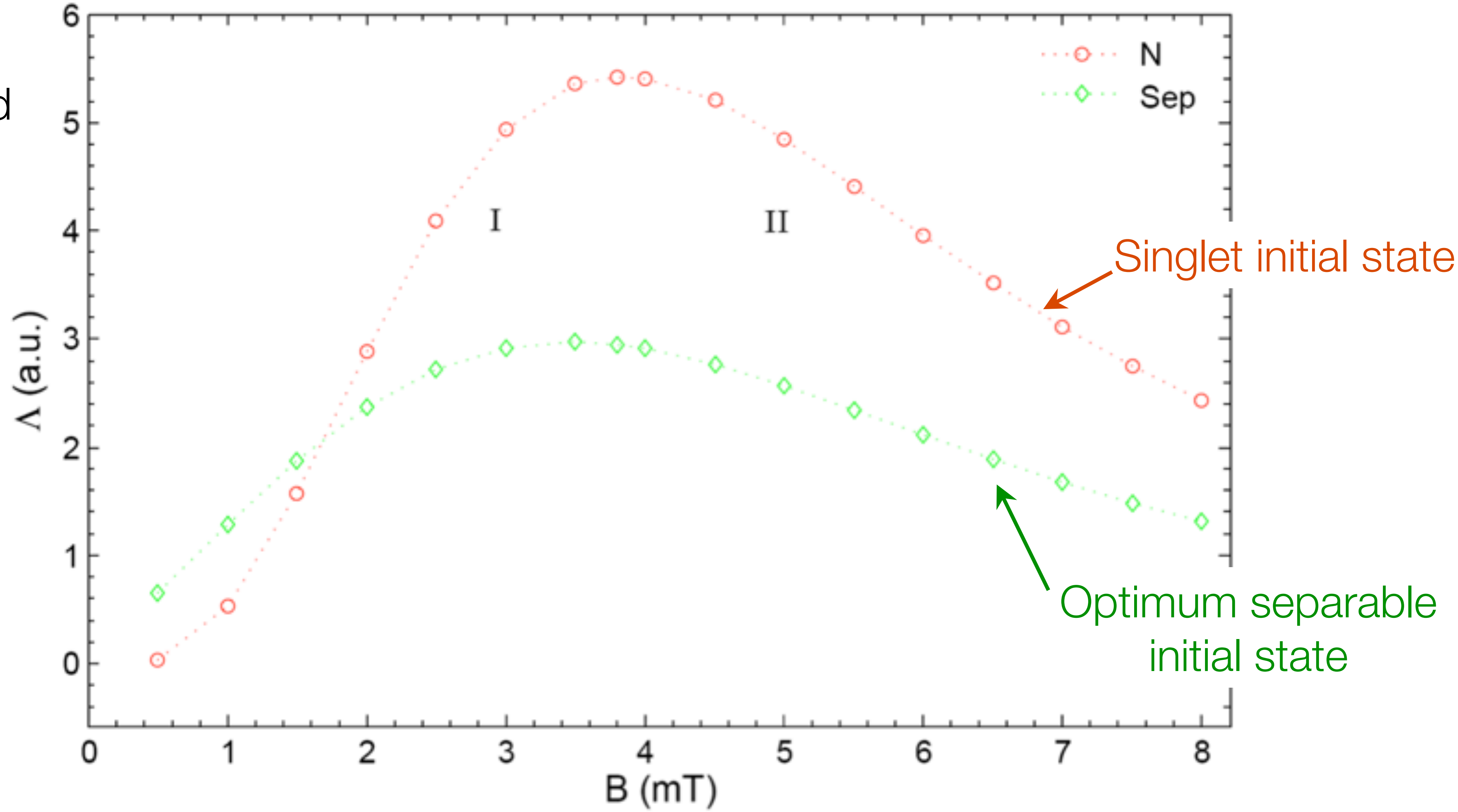
Is entanglement in the initial state relevant?

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

Optimum sensitivity for **singlet initial states:**

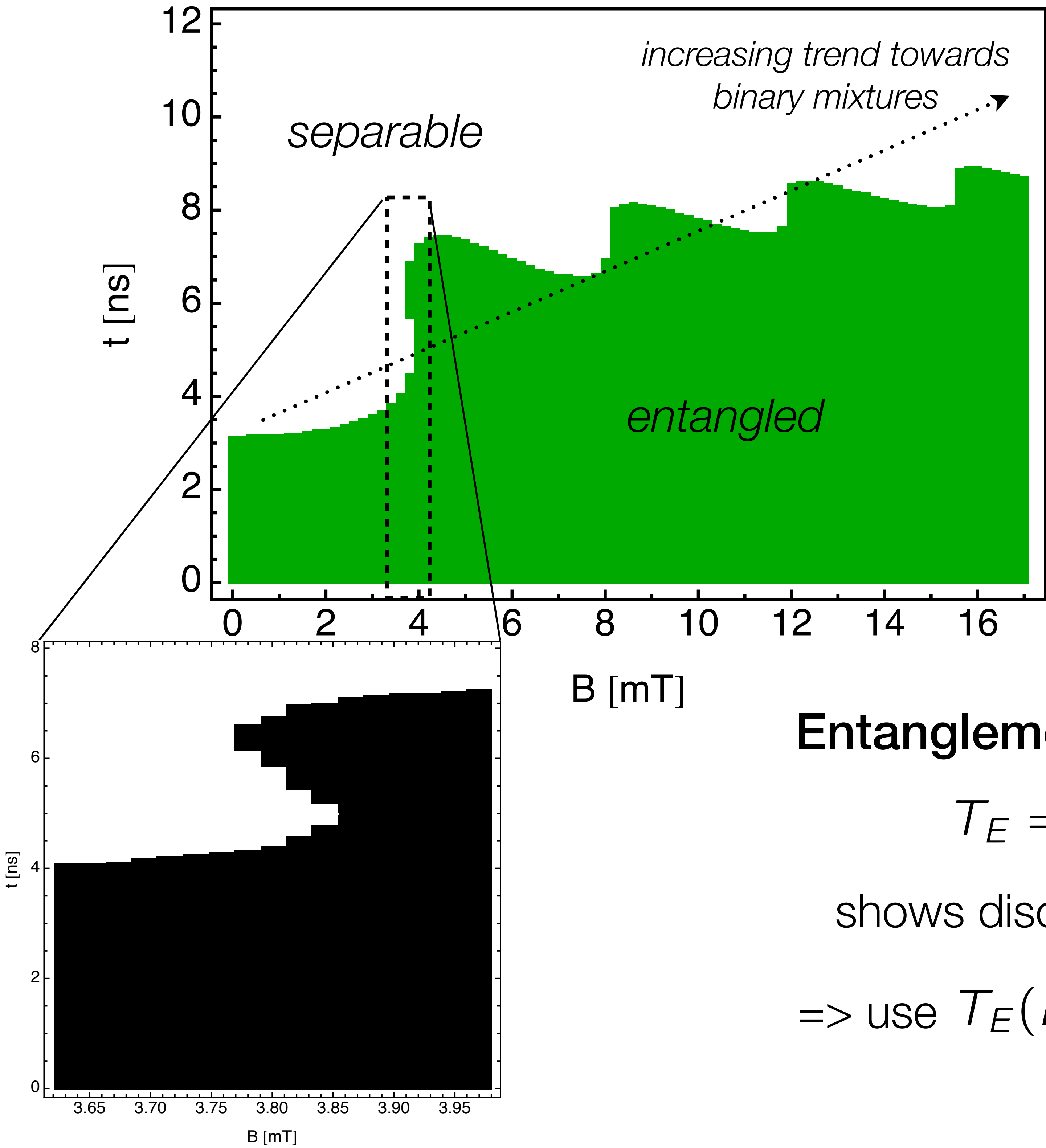
Magnetic field sensitivity:

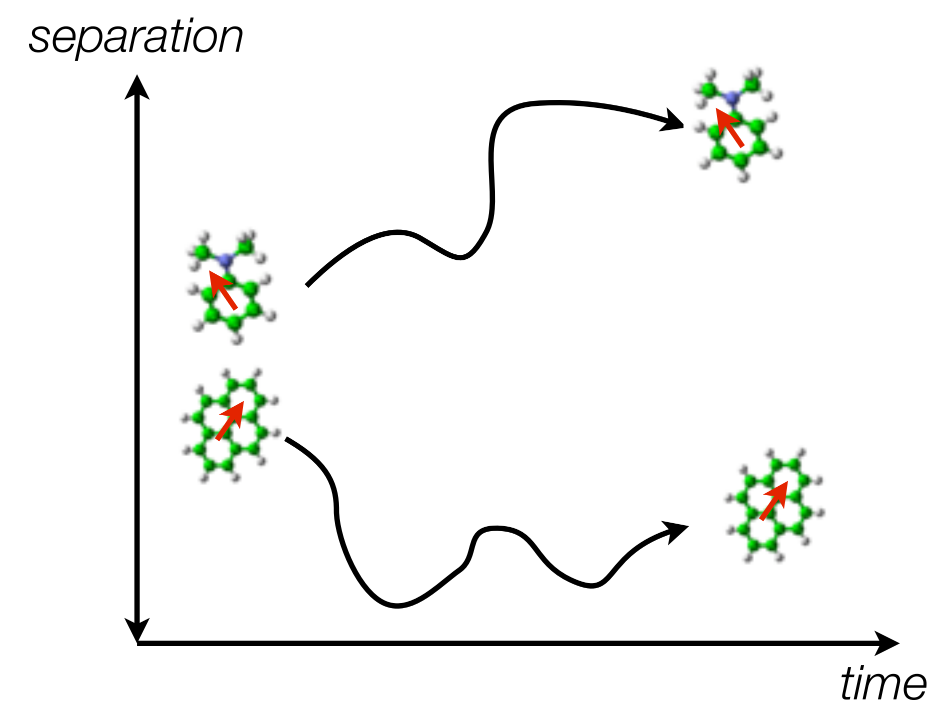
$$\Lambda_S(B) = \frac{\partial \Phi_S}{\partial B}$$



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

Entanglement lifetime of Py-DMA radical pairs





first observed in
Cai et al. *PRL* **104,** 220501 (2010)

Entanglement lifetime

$$T_E = \max\{t > 0 |\ \rho_{el}(t) \quad \text{entangled}\}$$

shows discontinuities due to (partial) revivals.

=> use $T_E(B)$ for magnetic field measurements

Entanglement measurement for radical pairs?

Challenge:

local observables of electron spins practically not accessible
(high B-fields or spacial resolution required)

Quantum control pulses affect both electrons in the same way

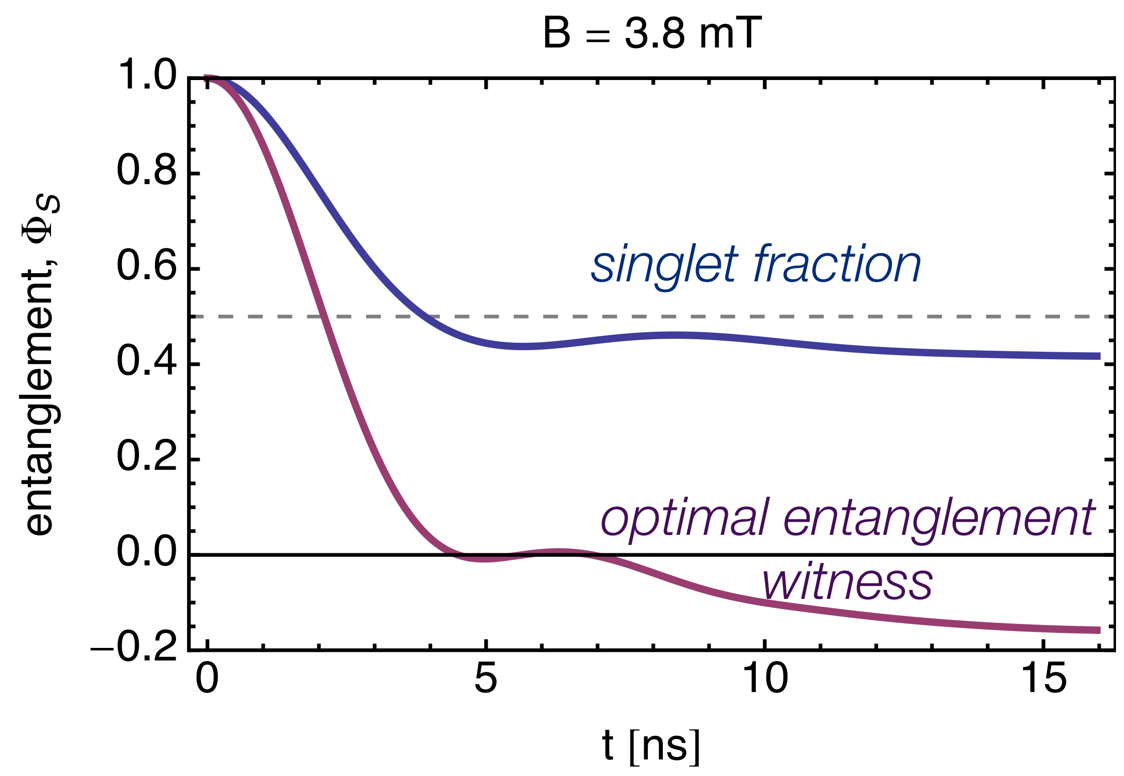
$$(U \otimes U)\rho_{\mathrm{el}}(U \otimes U)^{\dagger}$$

=> Which observables are accessible through fluorescence?

In Py-DMA only 3 parameters necessary for full tomography!

Entanglement quantified by concurrence:

$$C(\rho_{el}) = 2\max\{0, |c| - a\}$$



assumptions:

- locally maximally mixed
- isotropic HF-interaction
- no coherences between subspaces of different $S_z^{tot} = S_z^{(1)} + S_z^{(2)}$

$$\rho_{el} = \begin{pmatrix} a & 0 & 0 & 0 \\ 0 & b & c & 0 \\ 0 & c^* & b & 0 \\ 0 & 0 & 0 & a \end{pmatrix}$$

Entanglement witness for Py-DMA radical pairs

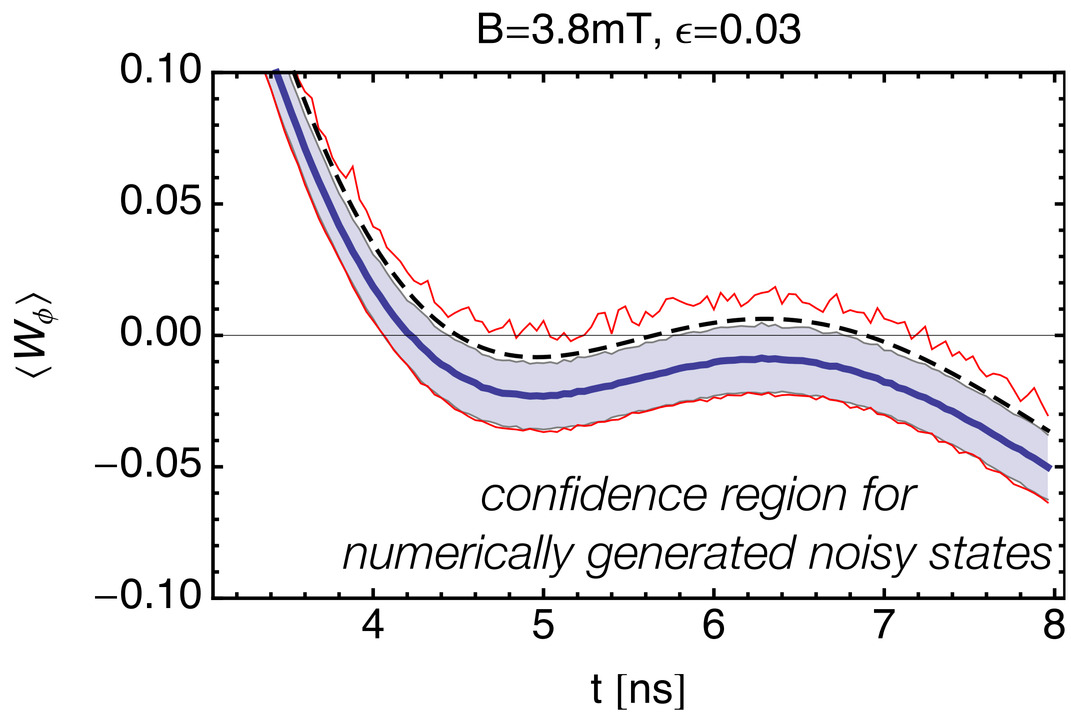
Optimal entanglement witness

$$W_\phi = 2|\phi\rangle\langle\phi| - 1$$

with

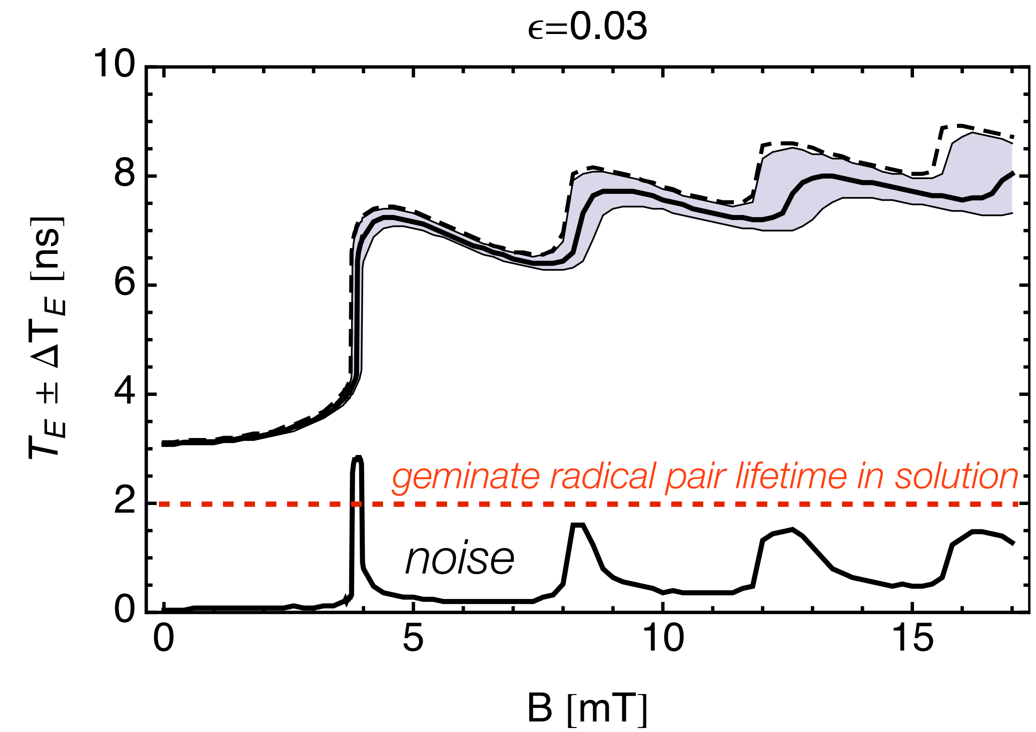
$$|\phi\rangle \propto |\downarrow\uparrow\rangle + e^{i\phi}|\uparrow\downarrow\rangle$$

$$\phi = \arg\langle\downarrow\uparrow|\rho_{el}(t)|\uparrow\downarrow\rangle$$



Radical pair spins entangled for

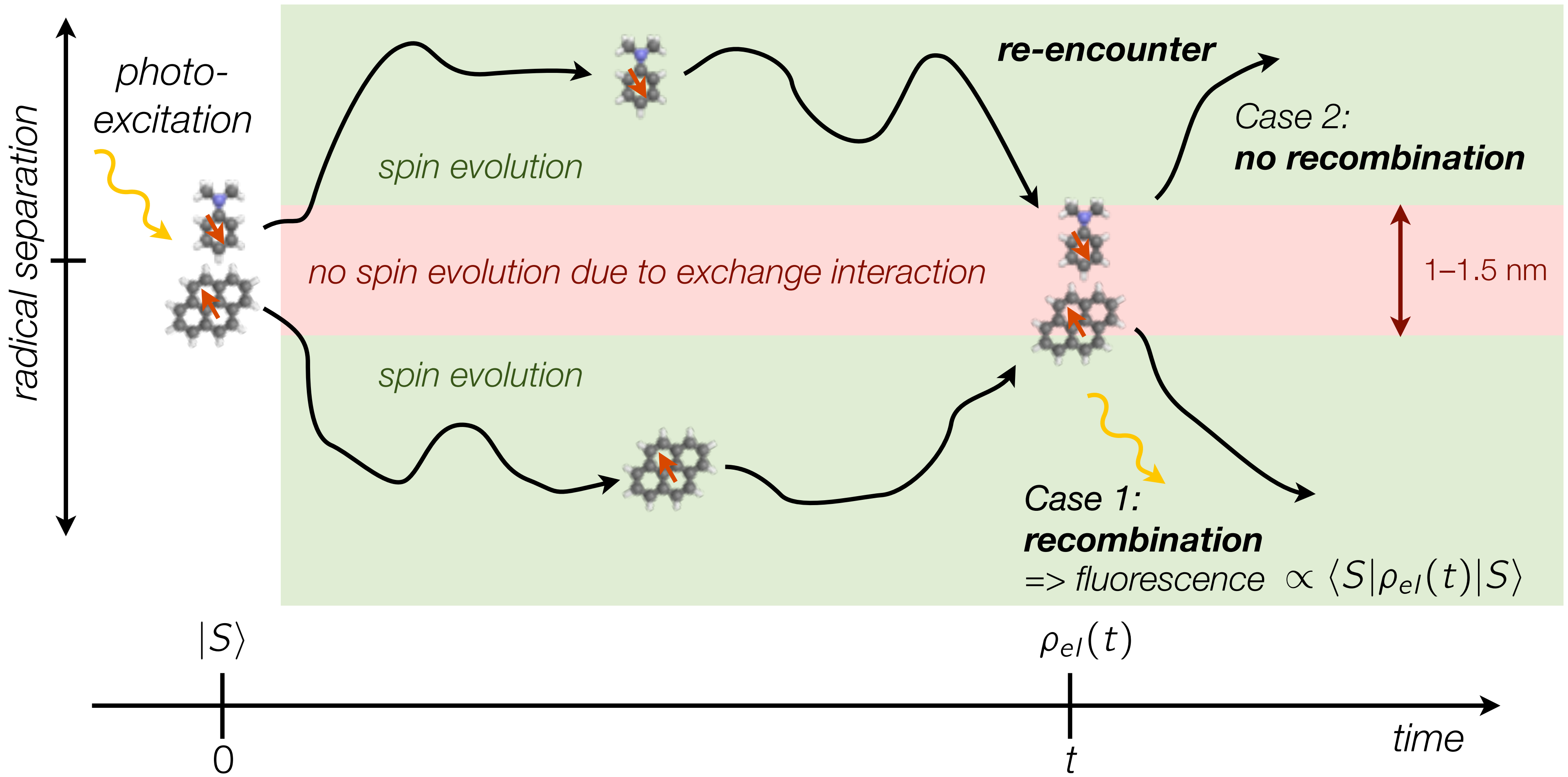
$$\mathrm{Tr}[W_\phi \rho_{el}(t)] > 0$$



Challenges:

- How to measure this witness?
- Radical pair lifetime ~2ns

Radical pair re-encounter dynamics



molecule diffusion imposes classical stochastic process of re-encounter events

total singlet product yield

$$\Phi_S(t) = \int_0^t d\tau \, \boxed{k e^{-k\tau}} \langle S|\rho_{\rm el}(\tau)|S\rangle$$

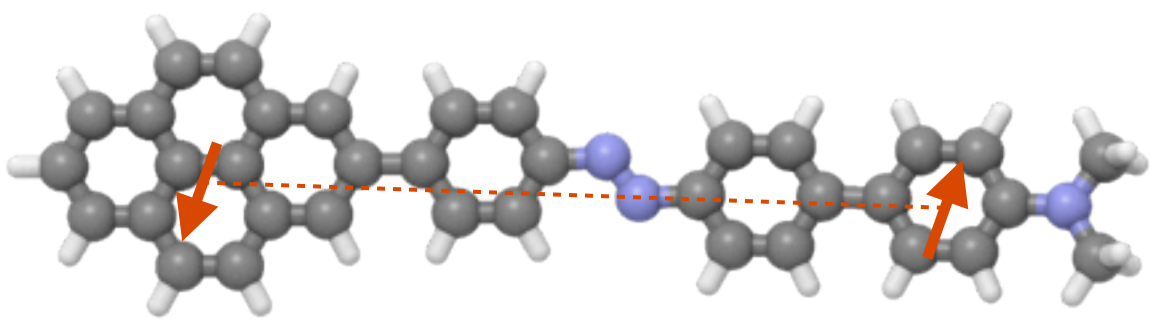
phenomenological reencounter probability

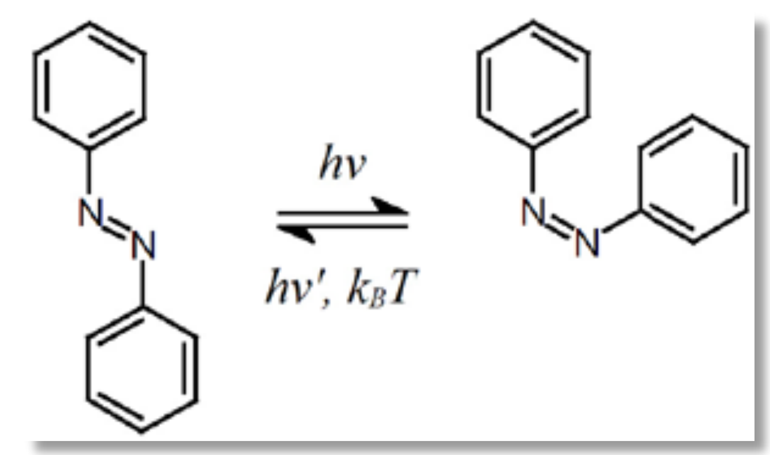
sensitivity

$$\Lambda(B) = \frac{\partial \Phi_S(t \to \infty)}{\partial B}$$

Controlling re-encounter with photo-switches

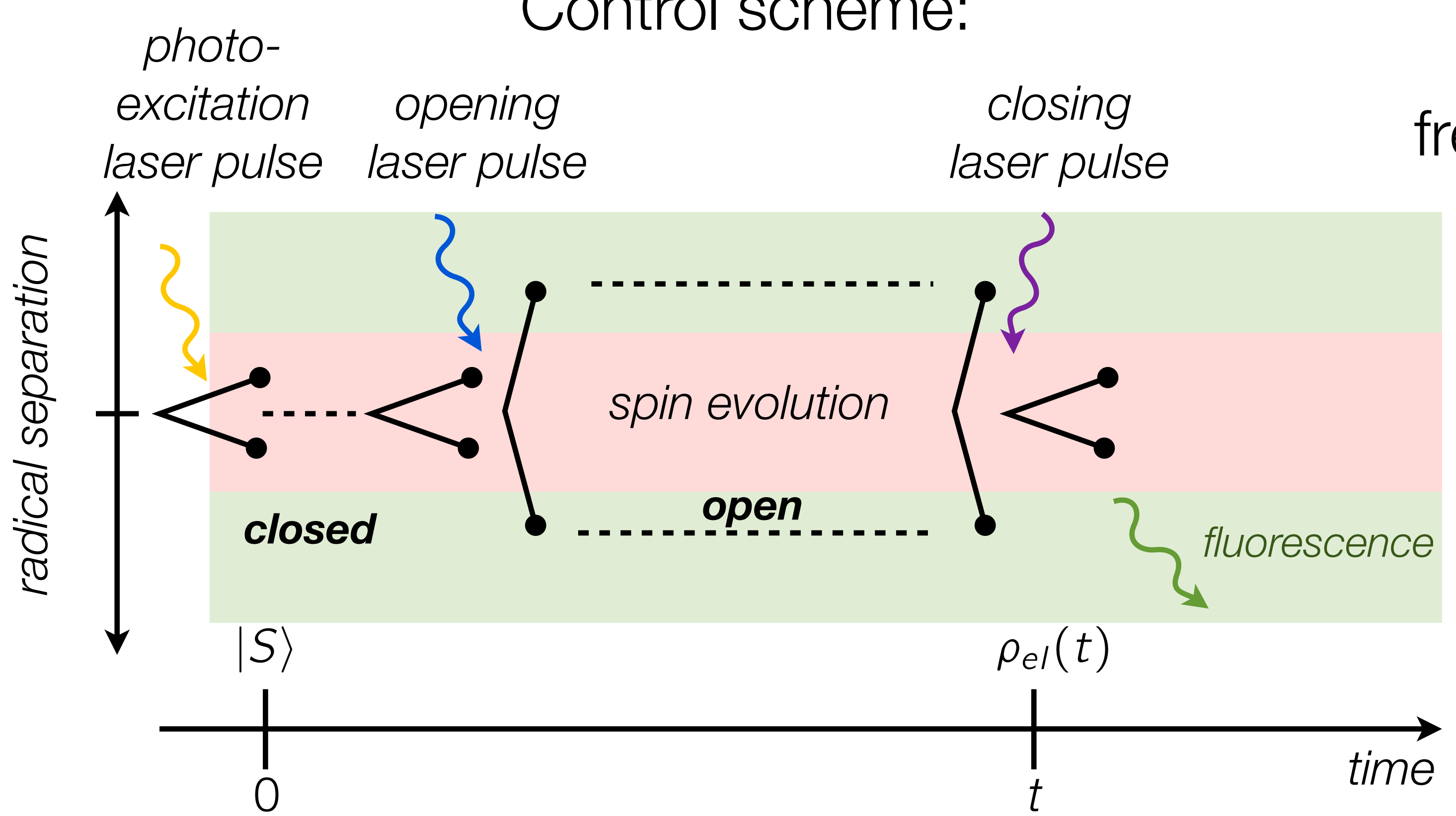
Mount radicals on photo-switchable bridge





azobenzene photo-switches change isomerization with a frequency dependence in absorption

Control scheme:



Control re-encounter probability distribution:

$$\Phi_S(t) = \int_0^t d\tau\, p_{\mathrm{re}}(\tau) \langle S|\rho_{\mathrm{el}}(\tau)|S\rangle$$

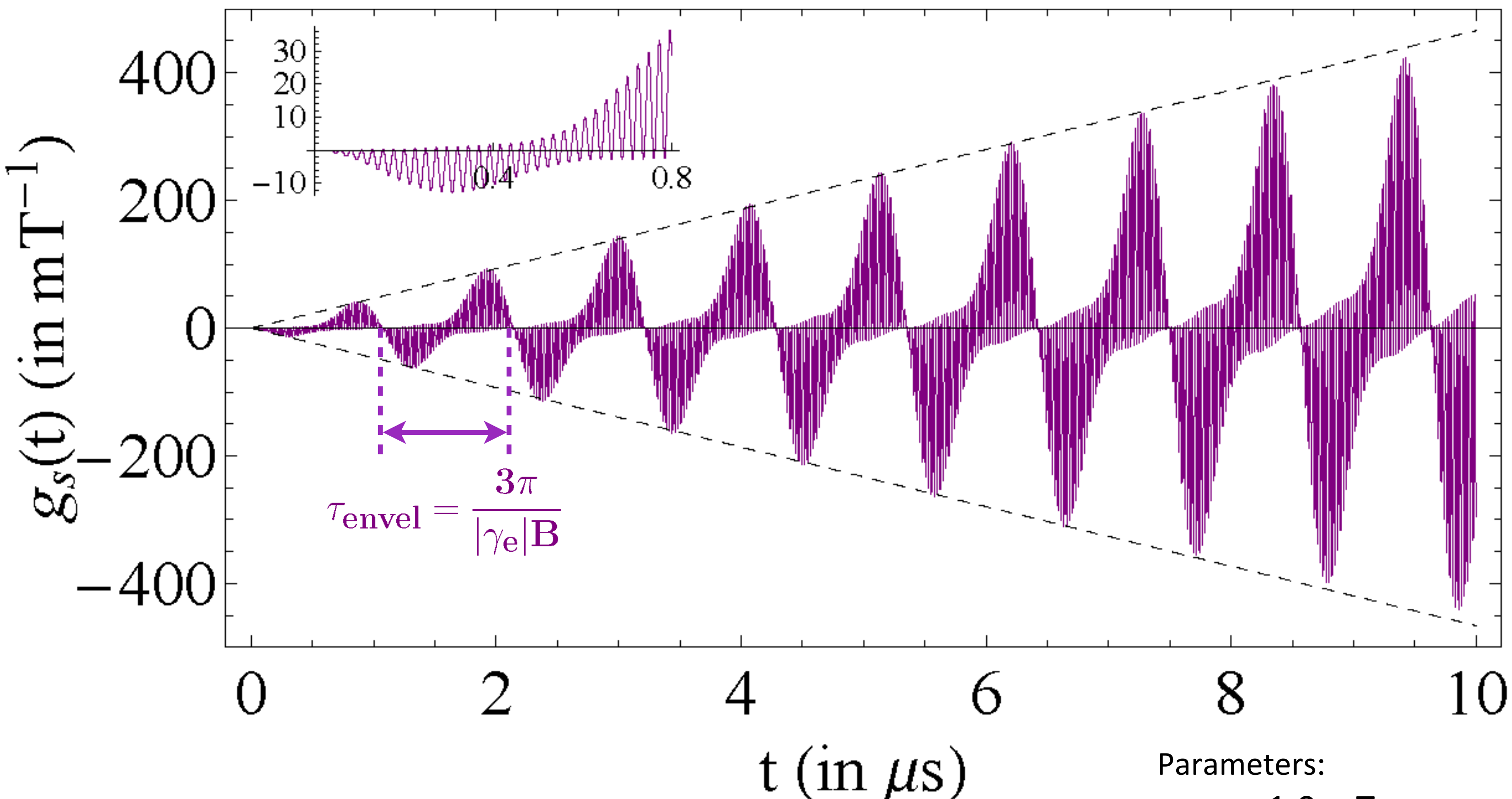
including multiple re-encounters...

arXiv: 1206.1280

Application to chemical magnetometry

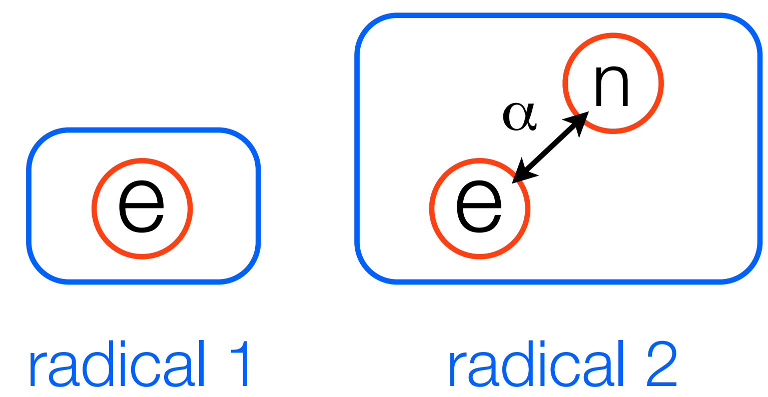
Magnetic sensitivity $\Lambda_S(B) = \frac{\partial \Phi_S(B)}{\partial B} = \int_0^\infty d\tau\, p_{\mathrm{re}}(\tau) g_S(B,t)$

instantaneous sensitivity $g_S(B,t) = \frac{\partial \langle S|\rho_{\mathrm{el}}(B,t)|S\rangle}{\partial B}$



Parameters:
α = 1.0 mT
B = 0.05mT

Model system of **2 electrons** and **1 spin-1 nucleus**



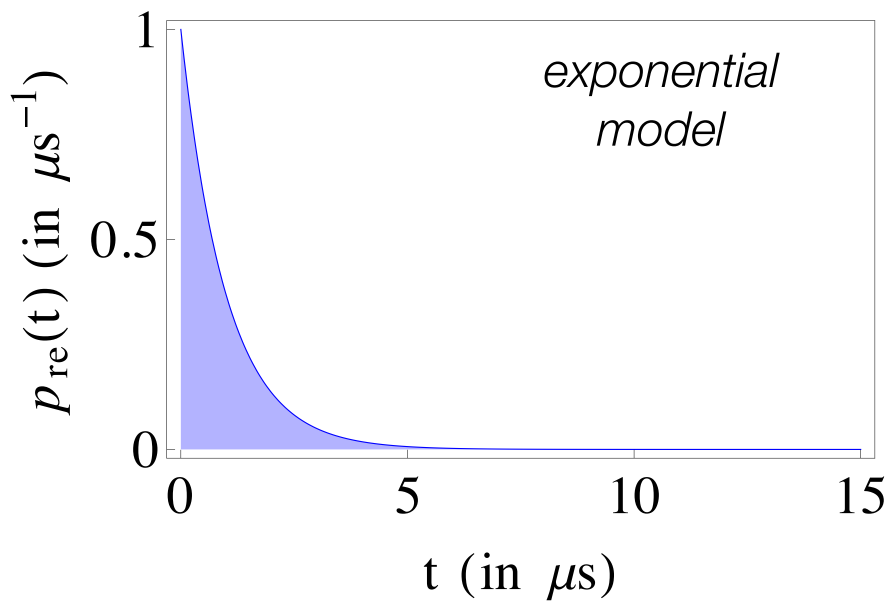
$H = -\gamma_e \vec{B}_{ext} \cdot (\vec{S}_1 + \vec{S}_2) + \alpha|\gamma_e|\vec{S}_2 \cdot \vec{I}$

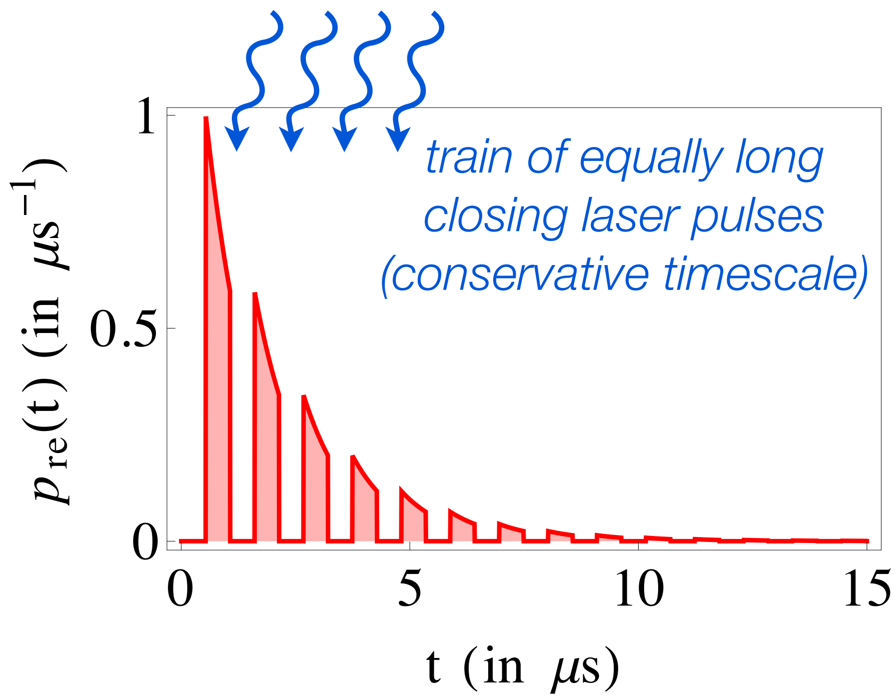
Initialize radical pairs and open photo-switch and...

For single nuclei molecules, see also:
T. Ritz et al., Biophys. J. 96 (2009)
J.-M. Cai, F. Caruso, and M. B. Plenio, PRA 85 (2012)

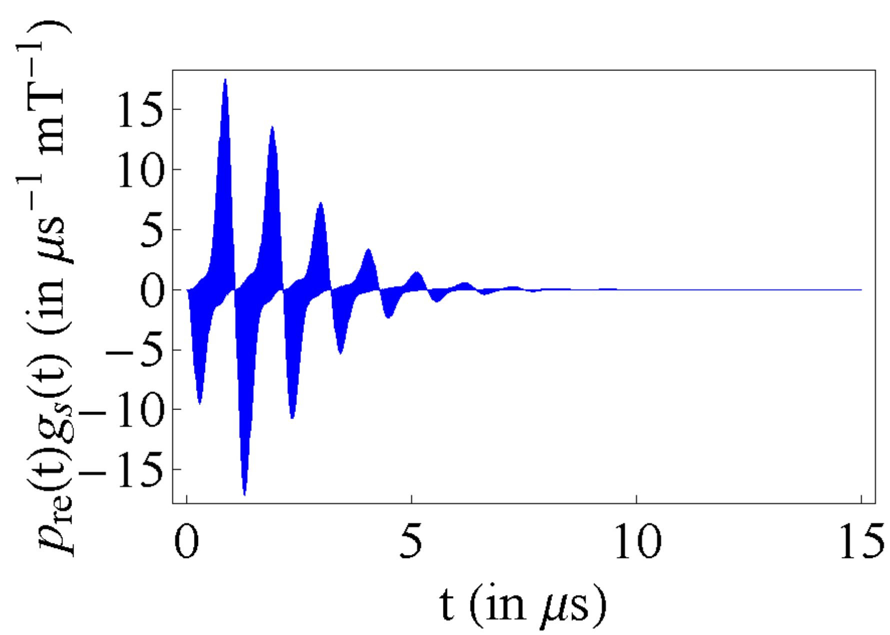
Engineering a re-encounter probability distribution

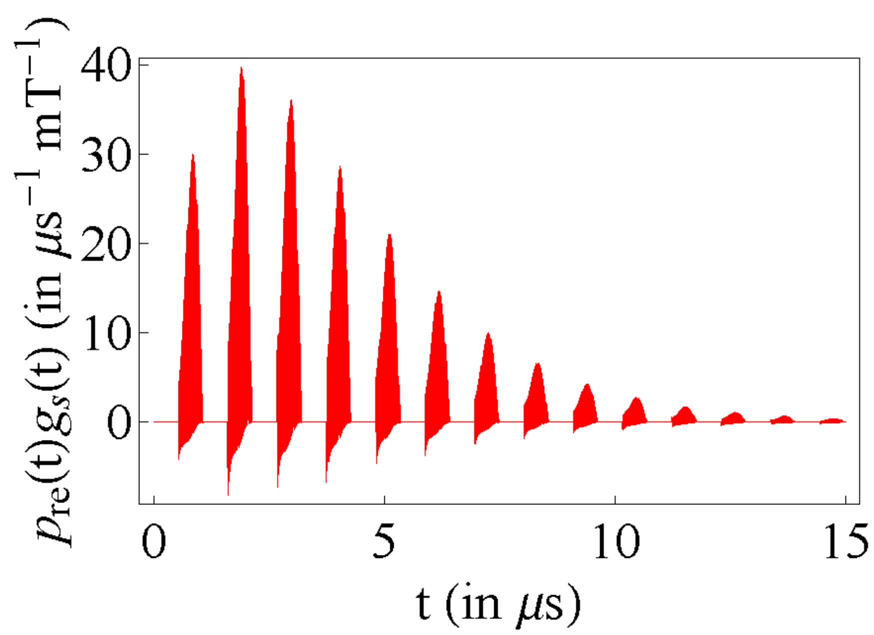
Re-encounter probability:





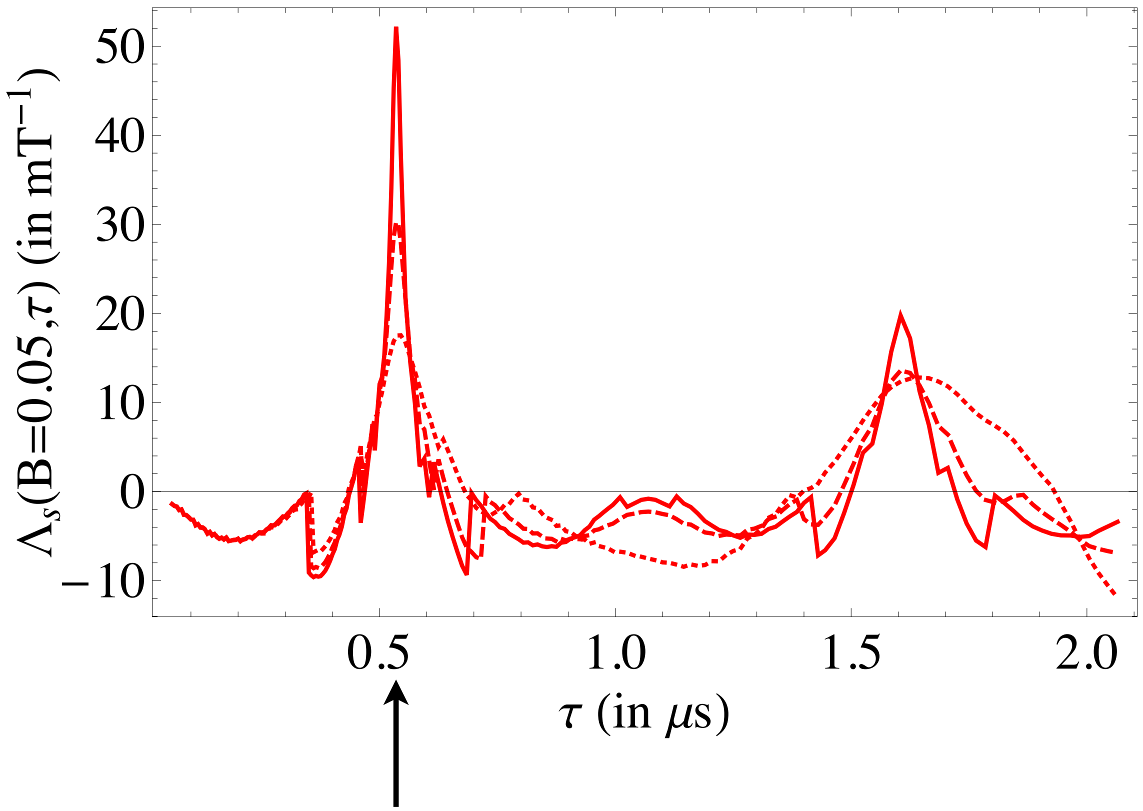
Integrand of magnetic sensitivity:





Finding the right laser-timing and the resulting sensitivity

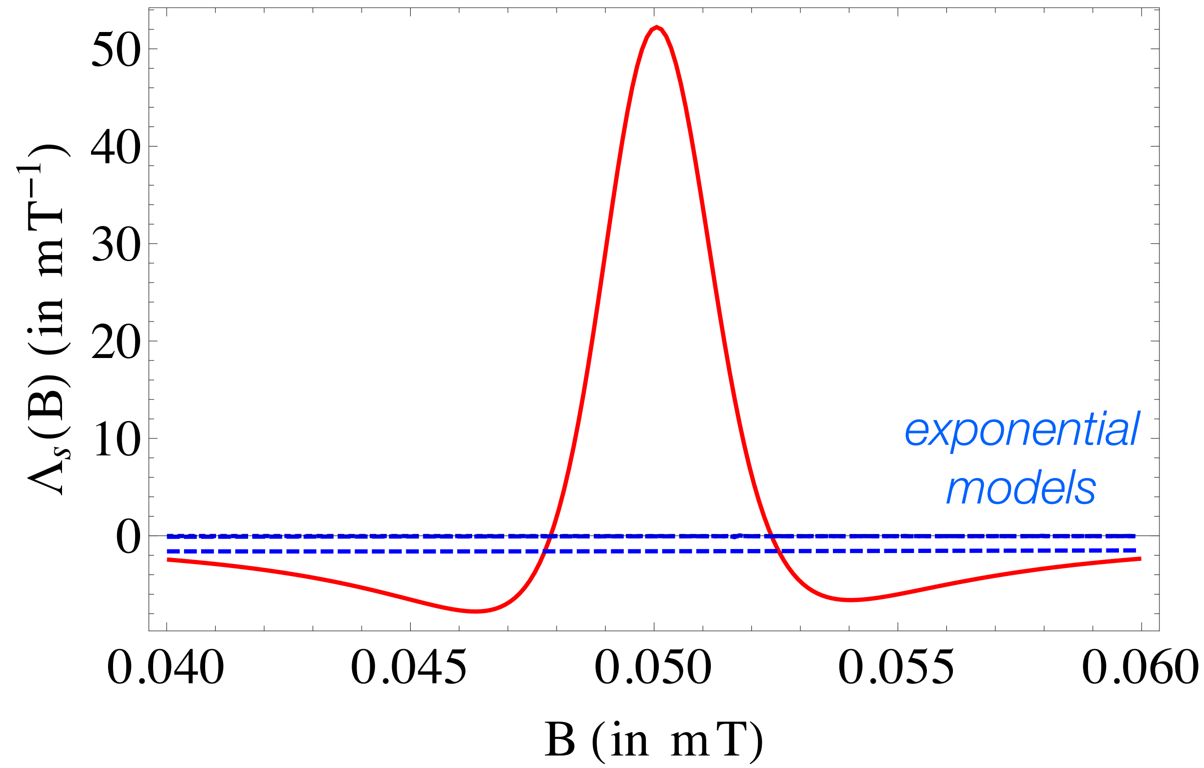
Sensitivity for different laser-timings



$$\tau = \frac{\tau_{\text{envel}}}{2}$$

Scanning over different laser-timings reveals resonances of increased sensitivity.

Sensitivity for optimal timing



Suitably controlled re-encounter probability enhances sensitivity for external (Earth-strength) magnetic field.

Summary

G. G. Guerreschi

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H. J. Briegel

- **Radical pair mechanism** is suitable for **chemical magnetometry** and is a logical candidate for animal magnetoreception.

- **Entanglement lifetime** of free radicals
(and perhaps other quantities showing revivals)
could be used for **magnetometry**.
(=> Which observables can be measured in principal using control techniques?)

- **Control of radical pair re-encounters** offers a new handle to **investigate reaction kinematics** in more detail and offers new strategy for **more sensitive chemical magnetometry**.

(↗ Guerreschi et al. arXiv:1206.1280)

Funding:

FWF Der Wissenschaftsfonds.

SFB FoQuS Foundations and Applications of Quantum Science