Optimal nuclear spin environment for a radical pair-based magnetic compass

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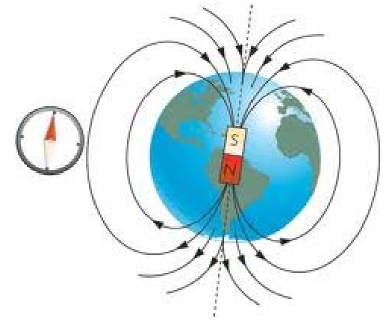
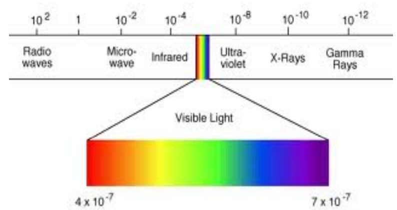
Radical Pair based Magnetoreception in Birds

The use of a magnetic compass by migratory bird **was first demonstrated for European robins by Wiltschko and Merkel** in **1966**
(Wiltschko and Merkel, Verh. dt. zool. Ges. 1966).



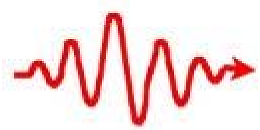
The suggestion that a light-induced **Radical Pair mechanism can act as chemical compass sensor** for magnetic orientation **was suggested by Schulten** et al. in **1978** (Schulten et al., Z. Phys. Chem. 1978).

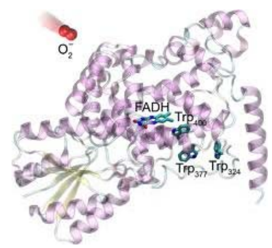
The evidence for an **ambient light-dependent** magnetoreception has been shown by **Wiltschko** et al. in **1993**
(Wiltschko et al., Nature,1993)



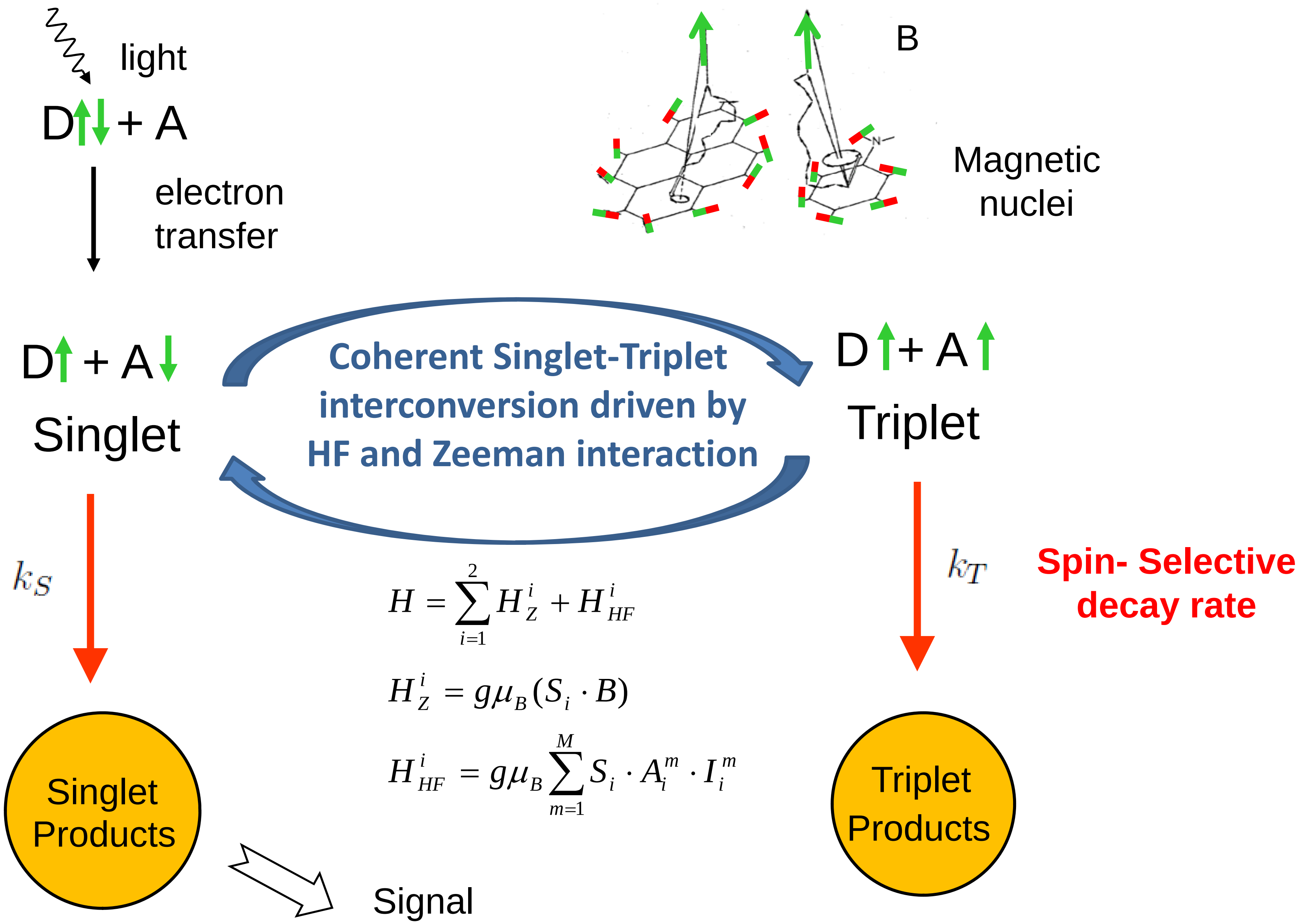
Vision-based magnetoreception

The proposal that a radical pair is created **photochemically** in the **bird's retina** by photoinduced electron transfer reaction in **an immobilized cryptochrome protein** was proposed by Ritz et al. in the 2000
(Ritz et al, Biophys J. 2000)





Photoinduced radical pair reaction scheme with magnetic field-dependent reaction products



$$H = \sum_{i=1}^{2} H_Z^i + H_{HF}^i$$

$$H_Z^i = g\mu_B (S_i \cdot B)$$

$$H_{HF}^i = g\mu_B \sum_{m=1}^{M} S_i \cdot A_i^m \cdot I_i^m$$

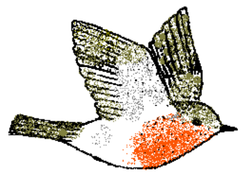
Calculating the Singlet Yield Φ_S

Stochastic Liouville equation

$$\dot{\sigma}(t) = -\frac{i}{\hbar}[H, \sigma(t)]_- - \frac{k_s}{2}[P^S, \sigma(t)]_+ - \frac{k_T}{2}[P^T, \sigma(t)]_+$$

Initial condition : singlet state

$$\sigma(0) = P^S / \mathrm{Tr}[P^S]$$



$F_S(t) = \mathrm{Tr}[P^S \sigma(t)]$ Fraction of radical pairs in the singlet state at any given time t

Φ_S **Amount of products decaying via singlet channel**

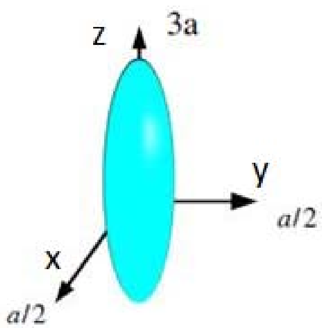
$$k_S = k_T = k$$

$$\Phi_S = \int_0^\infty k_S \, F_S(t) \mathrm{d}t \quad \longrightarrow \quad \Phi_S = \frac{1}{N} \sum_{m=1}^{4N} \sum_{n=1}^{4N} |P^S_{mn}|^2 \frac{k^2}{k^2 + \omega_{mn}^2}$$

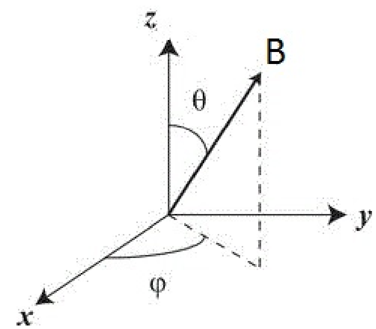
Spin independent decay rate

Anisotropic hyperfine *interactions* as source of orientation information

For a immobilized radical pair to be sensitive to different alignments to the magnetic field, it is necessary that the hyperfine interactions be anisotropic.

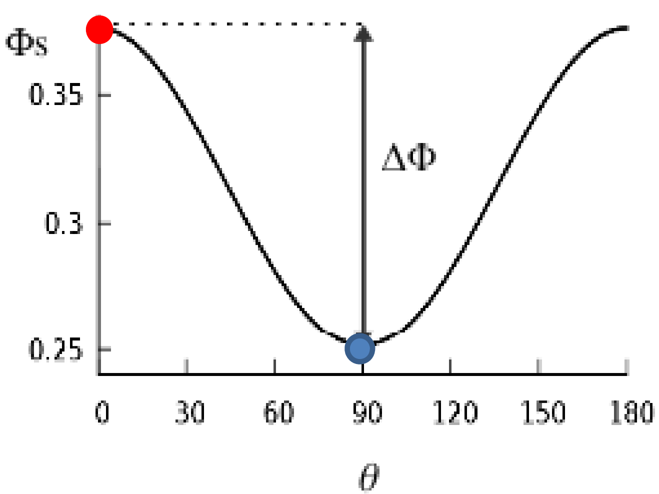


radical pair-fixed axis system



Angular sensitivity $\Delta\Phi = \Phi_S^{max} - \Phi_S^{min}$

Angular dependence of the singlet yield for one axial anisotropic hyperfine interaction



$$H = g\mu_B\left[(S_1 + S_2)\cdot B + S_1 \cdot A \cdot I\right]$$

$$A = \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix}$$

$A_x = A_y = a - a\cdot\alpha$

$A_z = a + 2a\cdot\alpha$

$\alpha = axiality$

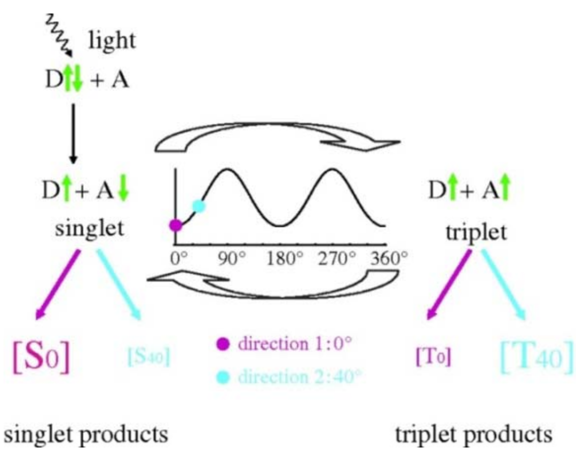
$$\Phi_S\ (B \ll a\ \ and\ \ k \ll a)\ =\ c_o + c_a\ \cos 2\theta$$

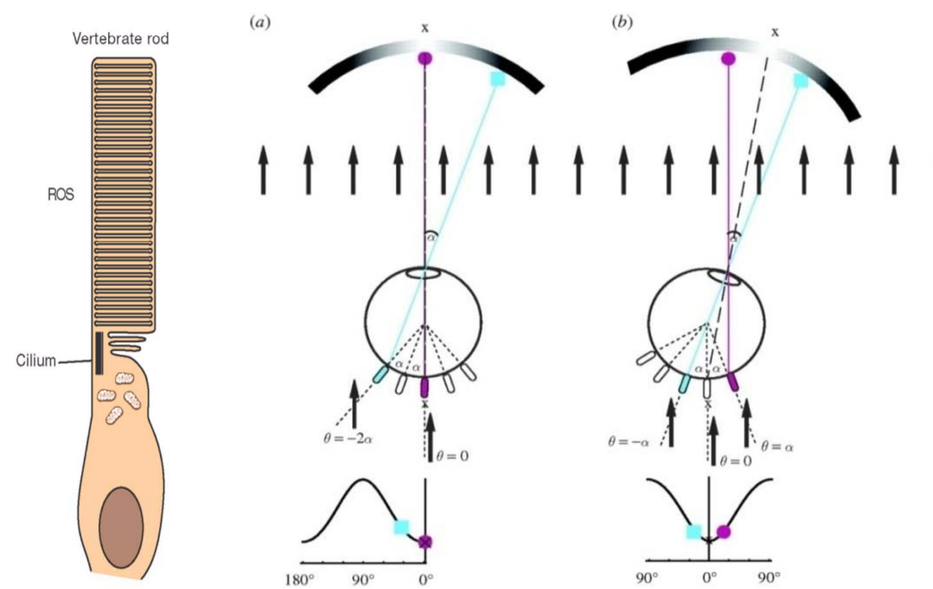
How does a bird make use of the angular dependence of one radical pair reaction yield ? It still remains unknown.... but

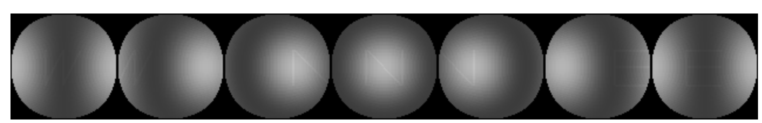
Magnetoreception is ambient light dependent → Radical Pair mechanism may be related to the visual system

We assume that many RPs reside orderly in photoreceptor cells on the retina and the reaction yields affect the sensitivity of those cells

Anisotropic HFIs give angular dependence of MFE for one RP





West  East

(K Wang, E Mattern and T Ritz, Phys. Biol, 2006)

Visual pattern

Factors determining directional magnetic field sensitivity

• Kinetics -> balanced rates are better

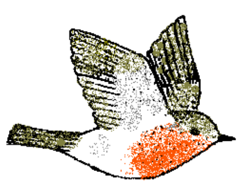
• Spin-correlation time -> needs to be long enough for MFE to occur

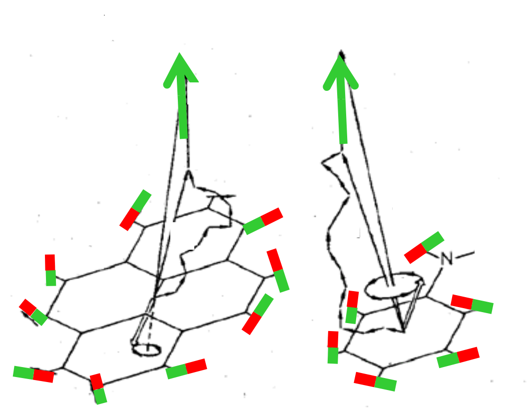
• Ordering -> fixed RPs optimal,
but even fairly disordered RPs can provide directional sensitivity

Lau et al., J. R. Soc. Interface, Hill and Ritz, *J. R. Soc. Interface*, Solov'yov et al. Biophys. J (2010)

• **Nuclear spin environment:**

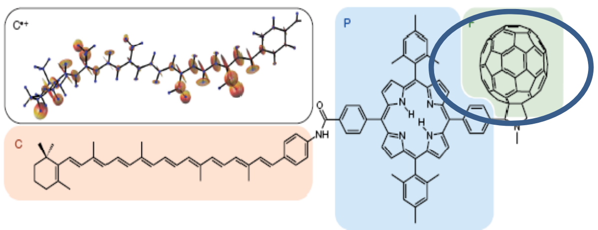
How should HFI be chosen so as to maximize sensitivity ?



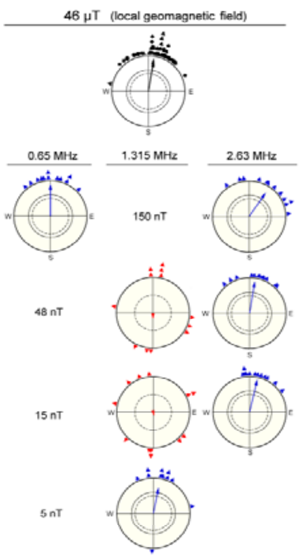


Nuclear spin environment: How should HFI be chosen so as to maximize sensitivity?

We study a special class of RP: One Radical has no HFI



First experimental demonstration of <u>earth-strength</u> MFE on a RP reaction used fullerene, with negligible HFI.
(Maeda et al. Nature 2008)



Behavioral experiments show strong resonance effects at free-electron Larmor frequency, observed in migratory birds. The presence of a very weak RF field at the Larmor frequency disrupts magnetic orientation .
(Ritz et al. Biophys. J. 2009).

This suggest a radical should be free of HFI in animal compass

Assuming this is true,
how should HFI on the other radical be arranged ?

One axial anisotropic HFI

$$H = g\mu_B\left[(S_1 + S_2)\cdot B + S_1 \cdot A \cdot I_1\right]$$

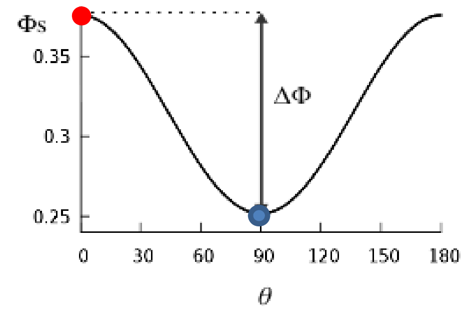
$$A = \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix}$$

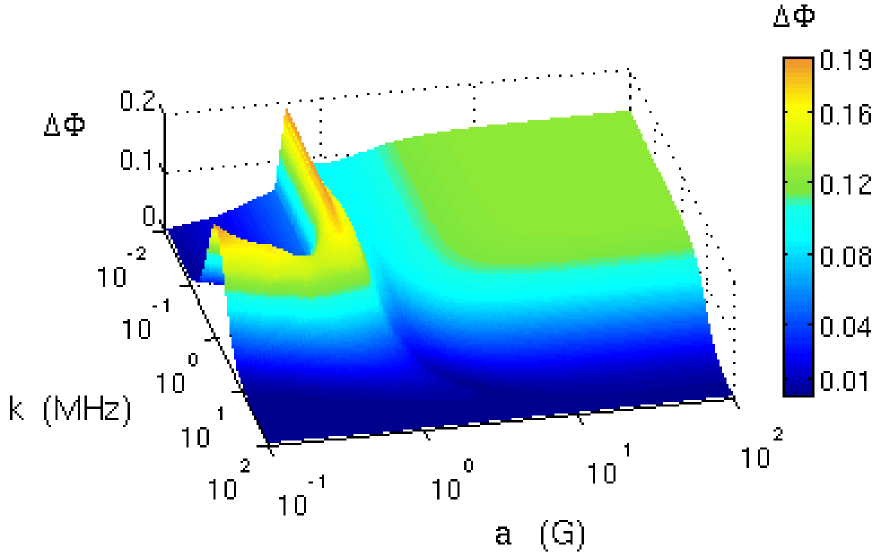
$$A_x = A_y = a - a\alpha$$

$$A_z = a + 2a\alpha$$

$$\alpha = 0.3$$

$$\Delta\Phi = \Phi_S^{max} - \Phi_S^{min}$$





For good directional sensitivity, the HFI strength needs to be large enough and the spin-correlation time needs to be long enough for directional MFE to occur.

Once one is above threshold, there is no change for larger values, the magnetic field effects are the same ⟶ robust

One axial Anisotropic HFI + one Isotropic HFI on the Same Radical.

We vary strength of isotropic HFI

$$H = g\mu_B\left[(S_1 + S_2)\cdot B + S_1\cdot A\cdot I_1^1 + a_{iso}S_1\cdot I_1^2\right]$$

$$\Delta\Phi = \Phi_S^{max} - \Phi_S^{min}$$

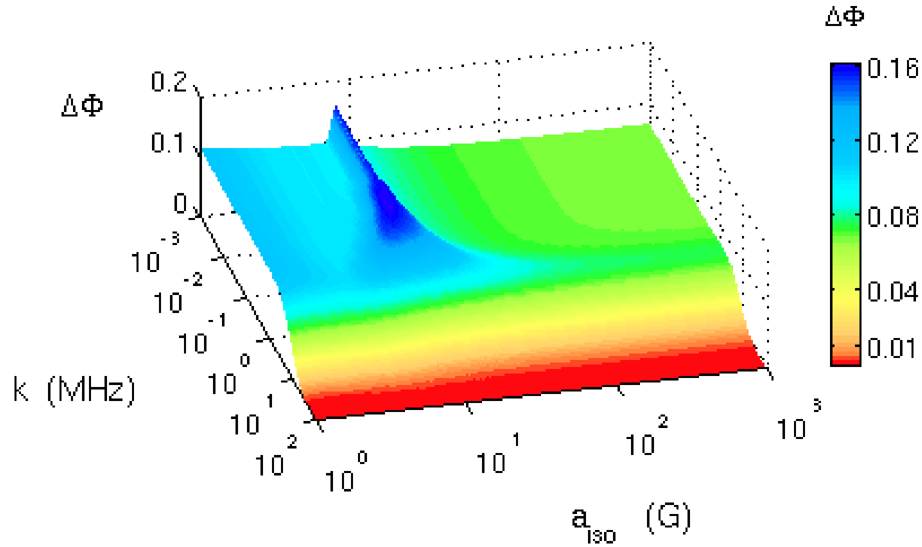
$$A = \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix}$$

$$A_x = A_y = a - a\cdot\alpha$$

$$A_z = a + 2a\cdot\alpha$$

$$a = 5G$$

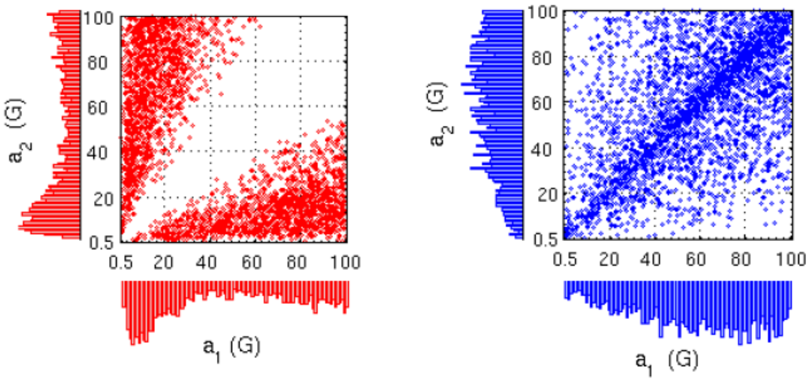
$$\alpha = 0.3$$

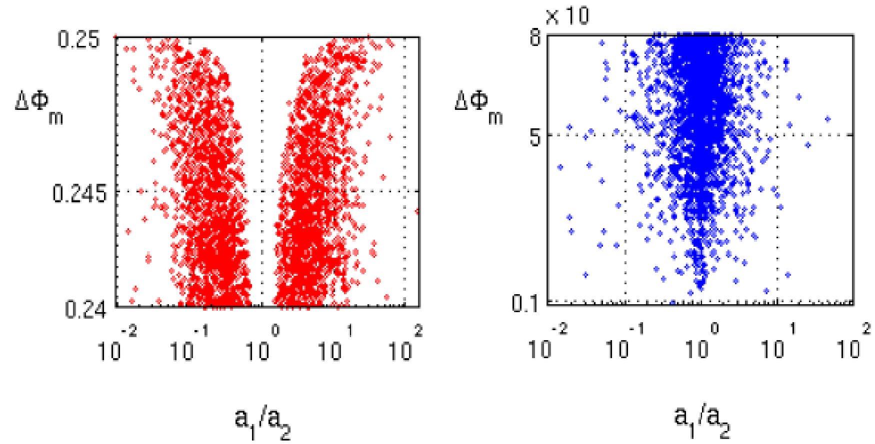


Note: presence of strong isotropic HFI does not destroy directional effects!

- simple arguments, based on strength of interactions only can be misleading

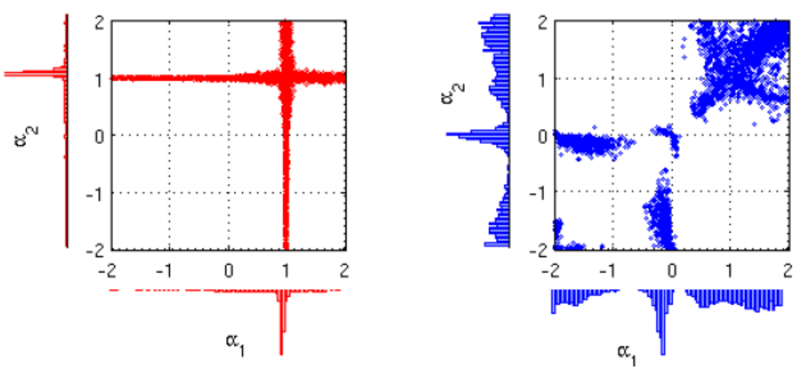
Two axial anisotropic HFI on the same radical:
10^6 RP randomly generated , pick 3000 best $\Delta\phi$, 3000 worst $\Delta\phi$, compare

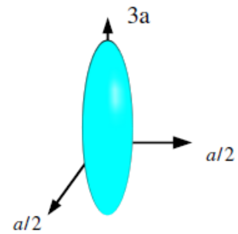




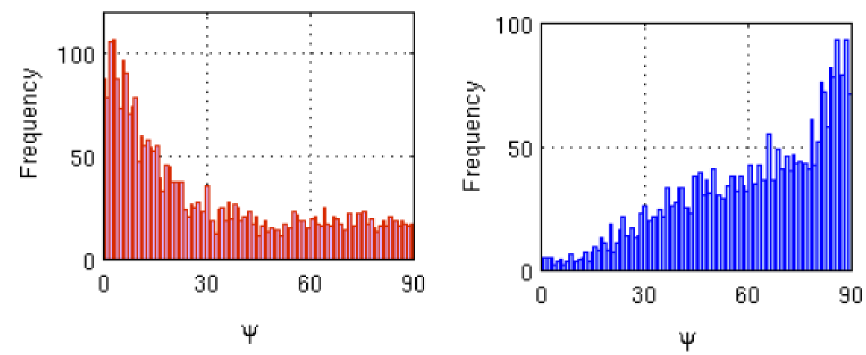
Strengths of HFI should not be the same, but not too different.

The ratio between the strengths should be roughly within one order of magnitude.





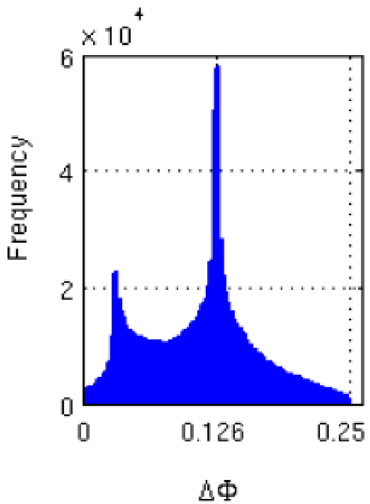
Larger axialities are better



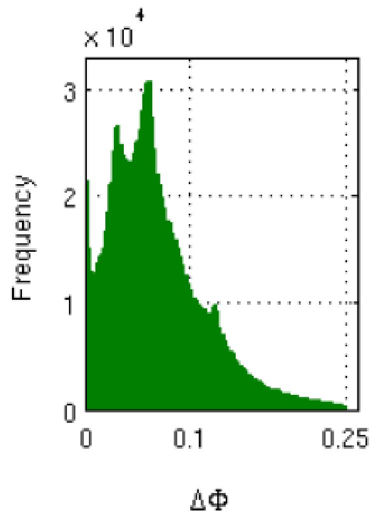
Axes should be collinear

Story seems to hold for RP with more HFI in the same radical

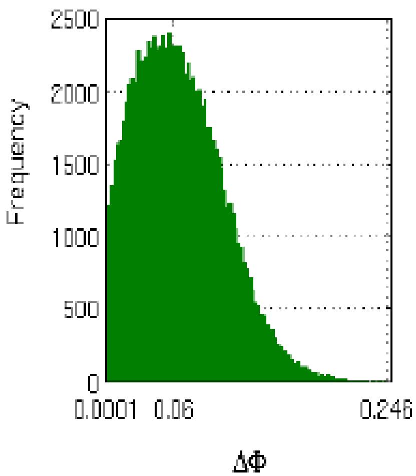
2 HFI: 10^6 RP



3 HFI: 10^6 RP



5 HFI: 10^5 RP (preliminary)

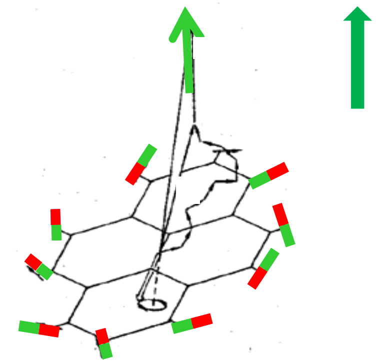


Arrangement of HFI is fairly forgiving: there are many arrangements that give directional sensitivity > 10%

It’s almost harder to find arrangements where there is very low directional sensitivity!

Not shown here: collinear axes, different strengths are somewhat better in all cases.

Optimal nuclear spin environment
Conclusions

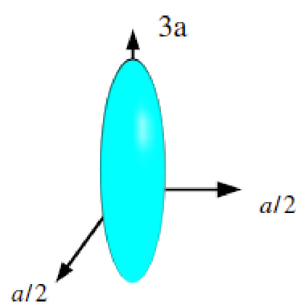


Assuming that one Radical should be free of HFI

How should HFI be chosen on the other radical so as to maximize sensitivity ?

- Strengths of HFI should not be the same, but strengths should be roughly within one order of magnitude

- Larger axialities are better



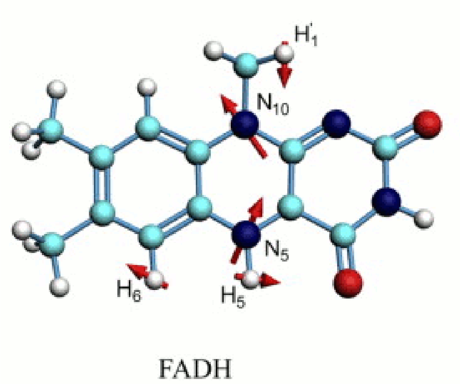
- Presence of other isotropic HFI is not very disruptive

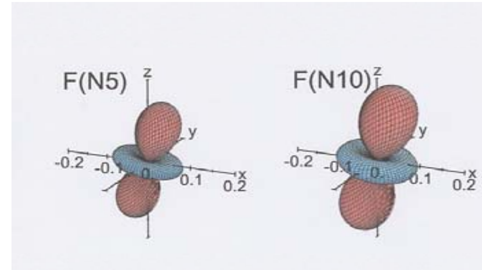
- HFI axes should be collinear

Biological Realization ?

Typical biological HFI are due to N, H, C-H3
with a comparable spread of strengths

Flavin matches the optimal radical well





(Cintolesi et al. Chem. Phys. 2003)

Realized in flavin, the active group of Cryptochromes. Cry has been suggested as the most promising photo-magnetoreceptor molecule (Ritz et al, Biophys J. 2000)

Radical partner with no HFI?

Suggestion of flavin – Reactive Oxygen Species (superoxide?) RP
(Ritz et al. 2009, Biophys J.)

If we find that the biological realization of RP-based magnetoreception is possible, we have an example of coherent quantum process in biology

Thank you for the attention

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